# INDUSTRIAL ORGANIC CHEMISTRY

ADAPTED FOR THE USE OF

MANUFACTURERS, CHEMISTS, AND ALL INTERESTED IN THE UTILIZATION OF ORGANIC MATERIALS IN THE INDUSTRIAL ARTS.

BY

#### SAMUEL P. SADTLER, Ph.D., LL.D.

CONSULTING CHEMIST; PROFESSOR OF CHEMISTRY IN THE PHILADELPHIA COLLEGE OF PHARMACY AND FORMER PROFESSOR OF ORGANIC AND INDUSTRIAL CHEMISTRY IN THE UNIVERSITY OF PENN-SYLVANIA; PAST PRESIDENT OF THE AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.

#### FOURTH EDITION

(REVISED, ENLARGED, AND RESET)



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## PREFACE TO THE FOURTH EDITION.

That over eleven years have passed since the previous (third) edition of this work was issued has been due to the fact that the author could not free himself at an earlier date from other literary and professional engagements sufficiently to take up the careful review of the field of industrial organic work required for a proper revision of this book.

Organic chemical industries have grown and developed greatly in the meantime, so that, although the same division of the subject-matter has been retained as one approved by experience, much new matter has been introduced in every chapter and many new technical products described and classified.

In some cases practically new industries have developed or are developing as new possibilities have been found for organic materials, as is seen in the artificial silk industry, the by-product coke-oven, the displacement of natural indigo by the synthetic indigo, and similar examples. The author has endeavored to present full and accurate statements of these new lines of manufacture.

While, as in previous revisions, the bibliography and statistics have been rewritten and brought down to date, it has been sought, in this revision, to make the sections on analytical methods fuller for some of the industries and to choose only such methods as are in present use and have been approved by the consensus of those directly interested as specialists in the several industries. At the same time we must recall the fact that the limitations of space have from the beginning precluded the thought of giving more than the most necessary methods, and these the author has given in concise form. There are numerous excellent analytical manuals or reference works on analysis, both of a general kind, like Allen's Commercial Organic Analysis, and special once on almost every separate industry. The titles of these latter will be found very generally in the several bibliographical lists under the appropriate chapter headings. Several new tabular statements have been incorporated and some new tables for reference have been inserted in the Appendix.

As in the preface of the first edition, the acknowledgments of the author are due to his friend, Mr. Louis J. Matos, for corrections and additions to Chapters XII, XIII, and XIV.

The author hopes that both chemical students preparing for entrance on practical work and manufacturers engaged in the development of our industrial resources will find assistance and benefit from the use of the book in its revised form.

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## PREFACE TO THE FIRST EDITION.

THE literature of Applied Chemistry is reasonably voluminous. have dictionaries and encyclopædic works upon the subject, a series of small hand-books for individual industries, and a mass of technical journals of both general and special application. Works, however, in which the effort is made to give within the bounds of a single volume a general view of the various industries based upon the applications of chemistry to the arts are much rarer, and especially is this true of works printed in the English language. In German we have Wagner's "Chemische Technologie," brought down to date by its present editor, Ferd. Fischer; Post's "Chemische Technologie," Bolley's "Technische-Chemische Untersuchungen," Heinzerling's "Technische Chemie," Ost's "Chemische Technologie," and others; in French, Payen's "Chimie Industrielle" and Girardin's "Chimie appliqué aux Arts Industriels," etc.; while in English we have only the now antiquated translations of Wagner and Payen. In speaking thus, the writer wishes to be understood as referring only to general works on chemical technology of moderate size. The excellent "Dictionary of Applied Chemistry," in three volumes, now being published by Longmans & Co., does not therefore come into the consideration, for the twofold reason of its size and of its encyclopædic and disconnected method of treatment.

Similarly, works which cover only a single side of the subject, like Allen's "Commercial Organic Analysis," are not referred to in the above statement.

The author has endeavored within the compass of a moderate-sized octavo to take up a number of the more important chemical industries or groups of related industries, and to show in language capable of being understood even by those not specially trained in chemistry the existing conditions of those industries. The present volume, it will be noticed, is limited to "Industrial Organic Chemistry." This field, while covering many very important lines of manufacture, does not seem at present to be so well provided for as the inorganic part of the subject. A companion volume, covering this other side of industrial chemistry, is in contemplation.

In taking up the several industries for survey, it has been thought desirable first to enumerate and describe the raw materials which serve as the basis of the industrial treatment; second, the processes of manufacture are given in outline and explained; third, the products, both intermediate and final, are characterized and their composition illustrated in many cases by tables of analyses; fourth, the most important analytical tests and methods

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are given, which seem to be of value either in the control of the processes of manufacture or in determining the purity of the product, and, fifth, the bibliography and statistics of each industry are given, so that an idea of the present development and relative importance of the industry may be had.

The author has endeavored in a number of cases to give a clearer picture of the lines of treatment for an industry by the introduction of schematic views of the several processes through which the raw material is carried until it is brought out as the finished product. A number of these diagrams have been taken from German and English sources, and several have been constructed by the author specially for this work. A list of these diagrams will be found appended.

A large number of the illustrations have been drawn specially for this work, and others have been procured from the best German and American sources.

Frequent foot references are made to authorities and sources of information, although this may not have been done in all cases. The author has in the analytical section made frequent use of Allen's "Commercial Organic Analysis," and hereby desires to acknowledge his special indebtedness to that most valuable work. He has also made frequent use of Wagner's "Chemische Technologie," thirteenth edition, and Stohmann and Kerl's "Angewandte Chemie." Besides these works of a general character he has also consulted a large number of special works, the titles of which will be found in the bibliographical lists appended to each chapter.

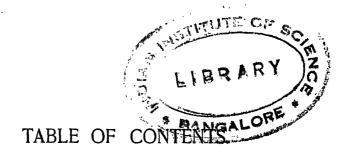
The author desires here to acknowledge his indebtedness to the many friends who have aided him by information and helped him especially in the collating of the statistics of the several industries.

His special indebtedness is due to his friend and former pupil, Mr. Louis J. Matos, M.E., who aided him in the completion of Chapters XI. and XII., and to whom Chapter XIV. in its entirety belongs.

To his colleague, Professor Henry Trimble, of the Philadelphia College of Pharmacy, he is also indebted for information upon the subject of Tannin and Dye-woods, as treated in Chapter XIII.

The original drawings made for this work and the index are also due to Mr. L. J. Matos.

The author hopes that this work may prove of some value to those engaged in the several lines of manufacturing industry touched upon by showing the chemical nature of the materials which are handled by them, and of the change which these materials undergo in the course of treatment and preparation as marketable commodities; that it may be suggestive to those engaged in research or invention in connection with chemistry; and, lastly, that it may be found to possess some interest for the general reader or the student of scientific or economic topics.



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# INDUSTRIAL ORGANIC CHEMISTRY.

#### CHAPTER I.

PETROLEUM, MINERAL OIL, AND ASPHALT INDUSTRY.

#### I. Raw Materials.

THE raw materials of this industry are hydrocarbons and products derived from them by alteration, which occur associated together in nature. They may be gaseous, liquid, or solid, and very frequently all three of these physical modifications are found admixed in the same crude material. As, on the other hand, they occur at times separate and distinct, they will be separately noted.

1. Natural Gas.—Under this name is generally known now the mixture of inflammable gases that is found issuing from the earth in various localities. While it is chiefly in connection with the boring of wells for oil or salt, or as a constantly-forming product of decomposition in coal-mines, that it has been obtained, we find that it often occurs entirely independently of these. "Burning springs," as they have been termed, have been known from the earliest historical times. Those of Baku, on the Caspian Sea, are supposed to have been burning as early as the sixth century before Christ, and to have been a sacred shrine of the Persian fire-worshippers. The Chinese have employed natural gas for centuries in their salt-mines as a source of illumination. In the United States it was employed already in 1821, at Fredonia, New York, as a source of illumination, and for sixty years past has served as the fuel for the evaporation of brine at the salt-wells of the Kanawha Valley, West Virginia.

The gas exists in the porous rock reservoirs under great pressure, 900 lbs. per sq. inch closed pressure and 38 to 45 lbs. open pressure having been measured. Yields of 15,000,000 cubic feet and in extreme cases 32,000,000 cubic feet daily have been attained in Ohio gas wells. John F. Carll estimated in 1889 that the Murrayville gas field in Western Pennsylvania has produced in four years 438,000,000,000 cubic feet,

which compressed under 900 lbs. (60 atmospheres) pressure would occupy a storage space of 7,300,000,000 cubic feet.

In chemical composition, natural gas is relatively uniform. It consists essentially of methane (marsh-gas), the first member of the paraffin series of hydrocarbons, which may be accompanied by ethane, propane, and the members of the paraffin series next following methane. Small quantities of hydrogen, carbon monoxide, and dioxide have been found to be present at times, while nitrogen is apparently an invariable impurity. The following table gives the results of analyses of natural gases, made in 1886, by Prof. F. C. Phillips for the Second Geological Survey of Pennsylvania. The localities chosen are all in Western Pennsylvania, with the exception of Fredonia, New York, which is introduced because of its historical interest:

Constituents.	Fredonia,	Sheffleld,	Wilcox,	Kane,	Speechley, near	Lyon's Run,	Raccoon Creek,	Baden,	Houston, near
	New York.	Warren Co., Pa.	McKean Co., Pa.	McKean Co., Pa.	Oil City, Pa.	Murrysville, Pa.	Beaver Co., Pa.	Beaver Co., Pa.	Cannonsburg, Pa.
Paraffin hydrocarbons Olefine hydrocarbons Carbon dioxide Hydrogen Nitrogen	90.05 0.41 Trace. 9.54		9.41	90.01 0.20 Trace. 9.79	0.02 Trace. 4.51	Trace.	Trace. Trace. 9.91	12.32	15.80

With these may be compared the natural gas from two important petroleum-yielding localities in Europe, viz., Pechelbronn, in Alsace, and Baku, on the Caspian.

	Pechelbronn I. (Engler.)	Pechelbronn II. (Engler.)	Pechelbronn III. (Engler.)	Baku I. (Schmidt.)	Baku II. (Schmidt.)
Methane Olefines Carbon dioxide . Carbon monoxide Hydrogen Oxygen Nitrogen	78.6 4.0 2.2 8.0 	68.2 3.4 2.9 8.7 4.3 16.9	77.3 4.8 8.6 3.4  2.0 9.0	92.49 4.11 0.93 0.84 2.18	93.09 8.26 2.18  0.98 
	100.00	99.6	100.10	100.00	100.00

2. CRUDE PETROLEUM (syn. Erdoel, Naphtha, etc.).—Under this heading is included the liquid product which is obtained so abundantly in various parts of the earth, either issuing from the ground naturally

or gotten by the boring of wells through the overlying rocks to the oilbearing strata. The oldest and until recently the most important petroleum district of the world is the Appalachian field of Western Pennsylvania, extending from Allegany County, New York, through Pennsylvania, southwesterly into West Virginia and Eastern Ohio. While the oils found in this district may differ considerably in gravity, color, and undoubtedly in chemical composition, the differences are not fundamental, and with certain special exceptions the crude oils from various localities are all brought together by the pipe-lines and become mixed before going to the refineries. None of these Pennsylvania or West Virginia oils contain any appreciable amount of sulphur or other impurity which would require a modification of the general refining methods. The heavy oils of Franklin and Smith's Ferry, Pennsylvania, and some few other localities are so valuable for the manufacture of lubricating oils that they are collected and worked separately. The Pennsylvania crude oil has in general a dark greenish-black color, appearing claret-red by transmitted light, and varies ordinarily in specific gravity from 0.782 to 0.850, or, as it is frequently expressed, from 49° B. to 34° B. In chemical composition it is essentially composed of hydrocarbons of the paraffin series  $C_nH_{2^{n+2}}$ , the gaseous and the solid members of the series being alike held dissolved in the liquid ones, and smaller amounts of the hydrocarbons of the benzene series  $C_nH_{2n-c}$ . According to Markownikoff, confirmed by Mabery, Pennsylvania petroleum also contains hydrocarbons of a series  $C_nH_{2n}$ , which he termed "naphthenes," but which are now generally known as methylenes. Within recent years another important field has developed, viz., Ohio, which includes the two distinct districts, the Lima oil district and the Macksburg district. The former is by far the more important, but the product is peculiar in that it contains sulphur, and has an offensive odor similar to Canadian crude oil. Careful analyses made in the author's laboratory have shown that it contains on an average 0.42 per cent. of sulphur, combined in relatively stable forms not decomposed by simple distillation.\* Reference will be made to it in speaking of refining methods. Within recent years the extension of the Lima (or Trenton Limestone) oil-field westerly into Indiana has added to the production of this grade of oil. The most important localities in the United States, outside of the Pennsylvania and Ohio oil-fields, are Texas and California, in which latter State a blackish petroleum of rather heavier consistency than Pennsylvania petroleum is found quite abundantly. This California petroleum is peculiar in containing nitrogenous bases of the pyridine and quinoline groups, and in leaving, instead of paraffin, an asphaltic base or residuum.

The Texas oil differs radically from Pennsylvania oil in being com-

<sup>\*</sup>Mabery identified in Ohio petroleum methyl, ethyl, normal propyl, iso- and normal butyl, pentyl, ethyl-pentyl, and hexyl sulphides and later other compounds of the formula C<sub>n</sub>H<sub>2</sub>nS to which he has given the name of "thiophanes."

posed chiefly of methylene hydrocarbons. It does not yield much burning oil distillate and contains as much as 2 per cent. of sulphur, part of which exists as free sulphur in solution. The residue is asphaltic.

Still more recent than the Texas oil development is that of the Midcontinent field, including specially Kansas and Oklahoma. The oil from this field varies greatly, and sometimes contains both an asphalt and a paraffin base.

Closely related to the Pennsylvania and New York oil-fields is the oil district of Canada. This is in the neighborhood of Enniskillen, in the western section of the province of Ontario. The Canadian petroleum, however, is distinctly different from that of Pennsylvania. It is darker in color, heavier in gravity, and is of a very offensive odor on account of sulphur impurity, and is therefore more difficult and expensive to refine. As before stated, it finds a counterpart in the oil of Lima, Ohio.

Second in importance to the Pennsylvania oil-fields, and even more prolific in the yield of individual wells, is the Russian petroleum district of Baku, on the Caspian. For detailed accounts of the extraordinary production of these wells, the reader is referred to Boverton Redwood's "Petroleum and its Products," 2nd ed., vol. i, p. 7, or to Engler's articles in Dingler's Polytechnisches Journal, Bd. celx and celxi. The Russian petroleum has a higher gravity than the American, averaging 0.873, or 31° B., and has been found to be entirely different in its chemical composition, consisting for the most part of hydrocarbons of the series  $C_nH_{2n}$ , isomeric with the olefine series, and called "naphthenes." As will be seen later, this difference in chemical composition involves a difference in the refining results.

The most important of the other European petroleum-fields are those of Galicia, which produce a variety of oils, both light and heavy, either accompanying or independent of the ozokerite of the region, those of Hanover, which yield thick oils, varying in specific gravity from .862 to .910, and those of Alsace, which also yield oils predominantly heavy, and used chiefly for lubricants.

The Asiatic petroleum-fields are those of Burmah, which have long been known to be very rich, and which, under British control, will now be developed, and those of Rangoon, in India, the oils from which are thick and heavy, yielding much lubricating oil and paraffin, and those of Japan.

3. CRUDE PARAFFIN.—Under this head may be understood the more or less compact solid material which often accompanies crude petroleum, is deposited from it on standing, and in some cases is found in extensive deposits independently of it. Thus, a deposit of buttery consistency separates from some crude oils, such as Bradford oil, and adheres to the pumping machinery and derrick, forming a crust which has to be scraped off from time to time. The same oils deposit crude paraffin in the pipe-lines, necessitating a periodical scraping of the interior of the pipe-lines. Much of the deposit which accumulates in the storage-tanks of crude oil is of the same material.

More important, however, is the occurrence of solid native paraffin, under the name of "ozokerite," or earth-wax. The best-known locality for this native paraffin is Boryslaw, in Eastern Galicia, although it is found also in the Caucasian oil district, and in Persia under the name of "neftgil," and some years ago was found in Southern Utah, in the United States. In color it varies from dark green to black, and possesses a lamellar or conchoidal fracture, according to the variety. It fuses between 56° and 74° C., or even higher. In chemical composition it does not differ much from the separated paraffin of petroleum oils.

4. BITUMEN AND ASPHALT.—We may have liquid bitumens, usually called *malthas*, and solid bitumens, called *asphalts*. Both may be considered as alteration products of petroleum hydrocarbons resulting from evaporation and oxidation.

Maltha (or mineral tar) was first found at Bechelbronn, in Alsace, and was studied by Boussingault, who described it as a viscid, tarry liquid of bituminous odor and a specific gravity of .966. It contains besides hydrocarbons both sulphur and nitrogen.

In the United States malthas are found in California in Kern, Ventura, and Santa Barbara Counties, as well as in Utah, Kentucky, Tennessee, and Texas. Those from California, which have been chemically examined, invariably contain some nitrogen present in the form of basic hydrocarbons. They also contain some water and dissolved gases.

The purest of the solid bitumens are known sometimes as "glance pitch" or "gum asphaltum." Prominent among them is gilsonite, which is found in the Uintah Indian reservation in Wasatch and Uintah Counties, Utah. The purity of this product (generally ninety-eight per cent. soluble in carbon disulphide) is such that it finds large application in the manufacture of varnishes and insulating compounds, the production being some three thousand tons annually.

Of solid asphalts, those of greatest commercial importance are the Trinidad Lake asphalt from the Island of Trinidad in the West Indies and the Bermudez asphalt from Venezuela, South America. The first of these contains in the crude state 39.83 per cent. of bitumen, 33.99 per cent. of earthy matter, 9.31 per cent. of vegetable non-bituminous matter, and 16.87 per cent. of water. After refining the water is eliminated and the bitumen is raised to about sixty per cent. The Bermudez asphalt contains but 2.63 per cent. of mineral matter and over ninety per cent. of bitumen. The solid asphalts of California contain from sixty to ninety per cent. of bitumen, while the mineral matter in most cases is a very pure silica, or in some cases infusorial earth. Other solid asphalts, but less valuable, are those of Cuba and Syria, containing some seventy-five per cent. of a hard, brittle bitumen.

Very important also are the bituminous limestones or "rock asphalts" of Europe. Among these may be mentioned those of Seyssel, France, Val de Travers in the canton of Neufchâtel, Switzerland, Ragusa in Sicily, and Limmer and Vorwohle in Germany. These contain from five and three-tenths to fourteen per cent. of bitumen, and about eighty-

six to ninety per cent. of carbonate of lime, and as they are largely used both in this country and in Europe in the manufacture of asphaltic mixtures or mastics, a table showing their exact composition is given:

	Seyssel, France.	Val de Travers, Switzerland.	Ragusa, Sicily.	Limmer, Germany.	Vorwohle, Germany.
Bitumen	8.15 91.80 .10 .15 .10	10.15 88.40 .30 .25  .45	8.92 88.21 .96 .91 .60	14.30 67.00 17.52	5.87 90.80 .85 .59 2.55
	100.00	100.00	- 100.00	100.00	100.00

In the United States the most important occurrence of bituminous limestone is that of Uvalde County, Texas, from which is obtained the product known as "litho-carbon," used in varnish-making and for insulating purposes.

Related to the natural asphalts are also such minerals as Albertite, from the Albert mines in New Brunswick, and the Ritchie mineral from Ritchie County, West Virginia.

The Torbane mineral, from Bathgate, Scotland, and Boghead coal, together with bituminous shales, also should be noted here. They form the crude material for the Scotch paraffin distillation.

#### II. Processes of Treatment.

1. OF NATURAL GAS.—If we refer to the composition of natural gas, as already stated, it will be seen that it is largely made up of methane and its homologues, with some nitrogen as impurity. The olefines, or "illuminating hydrocarbons" of ordinary coal-gas, are practically absent in most cases. This at once indicates quite clearly the value of natural gas as a fuel and its lack of value in the natural state for illuminating purposes. But that it can be readily converted into an excellent illuminating gas has been shown, and in Western Pennsylvania. where natural gas is abundant, it is being used for illumination as well as for fuel. To illustrate the treatment that is necessary for the purpose we may describe the McKay and Critchlow process, which has proven quite successful in practice. The apparatus consists essentially like the water-gas generators of a combustion-chamber filled with coal brought to a white heat by an air-blast and a fixing-chamber above filled with fire-brick, where the gaseous products of the first reaction combine with oil vapors to form a permanent illuminating gas. The procedure is as follows: The fuel having been rendered thoroughly incandescent, and the fire-brick structure having been heated to a light orange tint, the air-blast is shut off, the lid of the cupola closed, and the gas outlet opened. Natural gas is then introduced into the ash-pit

#### PROCESSES OF TREATMENT.

and forced up and through the incandescent fuel-bed, depositing i carbon on the surfaces of the fuel as decomposition is effected, as hydrogen gas is thus liberated, which, passing up through the operamber, meets the vapors of the hydrocarbon, which are projected in the chambers by means of a steam- or gas-injector. All of these product of decomposition passing together into the upper or fixing chamber, part of the hydrogen unites with the heavy hydrocarbons, producing the lighter hydrocarbons, while an intimate mixture of all the gases effected, forming a completely permanent illuminating gas, which pass off through the water-seal, condensers, scrubbers, and purifiers to the holder in the ordinary way. Natural gas is used quite largely now with Welsbach gas-mantles, and an excellent illumination is thus obtained.

The most recent industry based upon natural gas is the compressic of the gas by the aid of powerful compressors so as to liquefy the lea volatile portions and thus obtain a gasolene yield, as the great demar for gasolene for automobile, motor-boat and manufacturing purpos has caused a great demand for such a light fraction. What is calle "casing-head gas," that obtained in pumping crude oil, is best adapte. The gas from the deep wells of the California oil field are said to yie three gallons of gasolene per 1000 cubic feet of gas.

Natural gas is also burned for the production of a very pure grad of lamp-black. This manufacture, first carried out at Gambier, Ohio, now introduced at various places in the oil regions of Pennsylvani. The gas is burned from rows of burners placed in such position the flame impinges upon slate or metallic slabs or revolving cylinder and there deposits its carbon. In one building at Gambier, eighter hundred burners have been used, consuming two hundred and sevent five thousand cubic feet of gas per twenty-four hours.

2. Of Crude Petroleum.—As petroleum has been shown to be mixture of hydrocarbons of different volatility, the first operation wou naturally be to effect a partial separation of these hydrocarbons by process of fractional distillation. But, in fact, simpler lines of treatme were first tried. It was found that crude oils spread out over war water in tanks and exposed to the sun were much improved in gravi-This process was chiefly employed for the production and consistency. of lubricating oils, and the products were called "sunned oils." Th was followed by the application of methods of partial evaporation concentration in stills, either by direct application of heat or by the use of steam coils, carefully avoiding overheating. The products are calle "reduced oils," and form the best material for the manufacture of hig grade lubricating oils. They will be referred to again. The process which the great bulk of crude petroleum is submitted, however, is th of fractional distillation continued to the eventual coking of the redue. As the most valuable of the several distillates is that which is be used as illuminating oil, the percentage of that distillate obtainab is an important item in an oil refinery. A normally-conducted fra tional distillation of Pennsylvania petroleum will give from thirty-fi to fifty-five per cent. of oil suitable for illuminating purposes, and fro

twenty to thirty per cent. of lubricating oils. About 1865, however, it was found that if during the distillation the heavy vapors were made to drop back upon the hot oil in the still they became superheated and were decomposed. This process of destructive distillation or "cracking" allowed of a notable increase of the illuminating oil fraction at the expense of the lubricating oil. So at present some seventy-five to eighty per cent. of burning oil is obtained, while the residuum from which the lubricating oil is gotten is reduced to six per cent.

A general outline of the petroleum refining process as at present conducted is presented in tabular form on the accompanying diagram.

The Results of a Normal Distillation of One Hundred Cubic Centimetres of Crude Oils are thus given by Engler:

CRUDE OIL FROM	Sp. gr. at 17° C.	Began to boil.	Came over under 150° C.	Between 150° C. and 300° C.	Over 300° C.
Pennsylvania (I.) . Pennsylvania (II.) . Galicia (Sloboda) . Baku (Bibieybat) . Baku (Balakhani) . Alsace (Pechelbronn) Hanover (Oelheim)	0.8175 0.8010 0.8235 0.8590 0.8710 0.9075 0.8990		31.5 per cent. 26.5 per cent.	35 per cent. 47 per cent. 88 per cent. 39.5 per cent.	40.75 per cent. 33.5 per cent. 26.5 per cent. 39 per cent. 52 per cent. 47 per cent. 68 per cent.

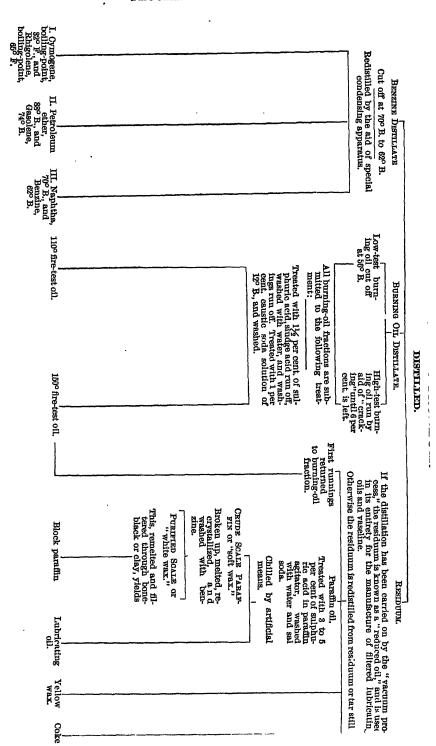
The Commercial Results usually obtained, on the other hand, are thus stated by the same authority:

CRUDE OIL FROM	Benzine and volatile oils.	Burning oil, Burning oil, first quality.		Residuum.	
Pennsylvania	10 to 20 3 to 6  4 10.5 5 to 6	60 to 55 to 35 to 60 to 40 27 to 33	65 45	5 to 10 80 to 40 55 to 60 25 to 35 36 50 to 60	

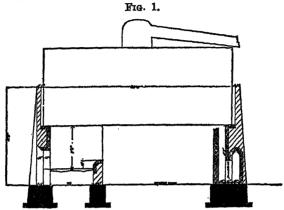
The process is generally divided into two quite distinct parts. The benzine and burning oil distillates are run from the same still, when the fluid residuum is transferred to what are usually called "tar-stills," in which the rest of the distilling operation is conducted.

The crude-oil stills are of two forms, the cylindrical still, as illustrated in section in Figs. 1 and 2, and the "cheese-box" still, although the latter is little used now. The former consists of a cylinder of boiler-plate, the lower half being generally of steel, thirty feet in length by twelve feet six inches in diameter. This still is set horizontally, as shown in the sectional view, in a furnace of brick-work, usually so constructed that the upper part of the still is exposed to the air. The "cheese-box" still has a body and dome-shaped top of boiler-plate and a double-curved bottom of steel plate. It is thirty feet in diameter and nine feet in height, and is set on a series of brick arches. The working charge of the cylindrical stills is about seven hundred barrels of crude

#### PROCESSES OF TREATMENT.

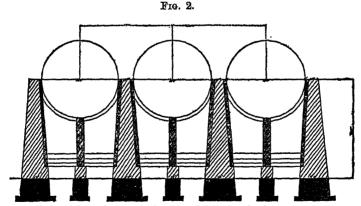


oil, although more recently stills of one thousand barrels capacity have been used. The still is usually provided with coils of steam-pipes, both closed and perforated. The steam, issuing in jets from the perforated pipe, has been found to facilitate distillation by carrying over mechanically the oil vapors.



Lateral vertical section of cylindrical still.

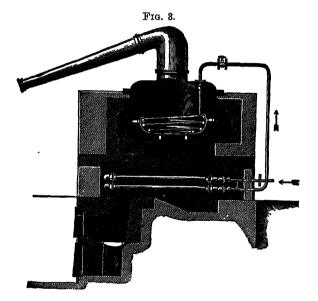
The condensing apparatus varies somewhat in the details of its construction, but consists essentially of long coils of pipe immersed in tanks, through which water is kept flowing. The terminal portions of the condensing pipes all converge and enter the receiving house within a few



Transverse vertical section of cylindrical still.

inches of each other. Near the extremity of each a trap in the pipe is made for the purpose of carrying away the uncondensable vapor. This may be allowed to escape, or is burned underneath the boilers or stills, effecting thereby a large saving in fuel. The condensing pipes generally deliver into box-like receptacles, with plate-glass sides, through which the running of the distillate can be observed, and from which test portions can be taken from time to time for the proper control of the process.

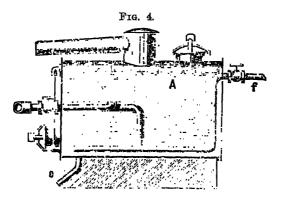
The tar-stills are usually of steel, cylindrical in shape, holding about two hundred and sixty barrels, and are set in groups of two or more, surrounded by brick-work. They are either upright or horizontally placed, usage inclining now to the latter position. Vacuum-stills have been and are still used to some extent, especially in the preparation of reduced oils for the manufacture of lubricants and products like vaseline. Of course, the evaporation in these stills takes place rapidly, and at the lowest temperature possible, insuring a fractional distillation and not a decomposition. If superheated steam be used, moreover, instead of direct firing, it is possible to reduce oils to 26° B. without any production of pyrogenic products. A still arranged with superheated steam is shown



in Fig. 3. Continuous distillation has not proved commercially successful in the United States. In Russia, on the other hand, continuous distillation has been eminently successful, being especially suited to Baku petroleum, as the quantity of burning oil separated being comparatively small, the residuum is not very much less fluid than the crude oil. The stills, each of the capacity of four thousand four hundred gallons, are arranged in groups or series of not more than twenty-five, as shown in Figs. 4 and 5, one of which is a front view, and the other a section, and a stream of oil is kept continuously flowing through the entire number. The crude oil, entering the first still, parts with its most volatile constituents; passing into the next still, has rather less volatile hydrocarbons distilled from it; and, finally, flows from the last still in the condition of residuum, which in Russia is termed astatki, or masut. The several stills are maintained at temperatures corresponding with the boiling-points of the products to be volatilized. Superheated steam is used for all the stills, the steam being delivered partly under the oil and

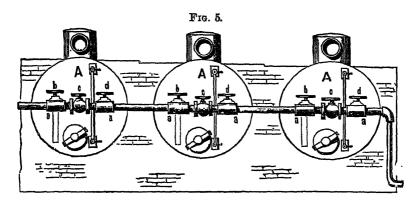
partly above the level of the oil,—that is, in the vapor space above. The fuel used under all the stills in Baku is petroleum residuum, or astatki.

To recur, now, to the products of the first rough distillation of crude oil, the first fraction, known as the "benzine distillate," and amounting usually to twelve per cent. of the crude oil, is redistilled by steam heat in cylindrical stills, holding five hundred barrels, and is sometimes separated



into the following products: cymogene, 100° to 110° B. gravity; rhigolene, 90° to 100° B. gravity; gasolene, 80° to 90° B. gravity; naphtha, 70° to 76° B. gravity; benzine, 62° to 70° B. gravity.

The time occupied in working the charge is about forty-eight hours. The percentage of these products varies, but, as a rule, amounts to about twenty-five per cent. of the first three collectively, rather more than



twenty-five per cent. of the naphtha, and about forty per cent. of the benzine. The deodorization of the benzine which is to be used for solvent purposes in pharmacy or the arts is effected somewhat after the manner to be described under burning oils by the action of sulphuric acid. Only the proportion of acid used is much smaller and the agitation is effected by revolving paddles instead of by an air-blast. One-half of one per cent. is sufficient in this case. Other processes have been proposed for the deodorization, such as the use of dilute sulphuric acid and potassium

permanganate, followed by sodium hydroxide, which oxidize the impurities and sweeten the product.

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The treatment of the illuminating oil fraction is a more important process. It must be freed from the empyreumatic products resulting from the distillation, which give it both color and disagreeable odor. To effect this it is subjected to a treatment with sulphuric acid, washing with water and a solution of caustic soda. This operation is conducted in tall cylindrical tanks of wrought iron, lined with sheet-lead, which are called "agitators." The bottom is funnel-shaped, terminating in a pipe furnished with a stopcock for drawing off the refuse acid and soda washings. The distillate to be treated must be cooled to at least 60° F., and before the main body of acid is added for the treatment, any water present must be carefully withdrawn. This is done by starting the agitation of the oil by the air-pump and introducing a small quantity This is allowed to settle, and withdrawn. The oil is now agitated, and about one-half of the charge of acid is introduced gradually from above. The agitation is now to be continued as long as action is indicated by rise of temperature, when the dark "sludge acid" is allowed to settle, and withdrawn. The remaining portion of acid is added, and a second thorough agitation takes place. The whole charge of acid needed for an average distillate is about one and one-half to two per cent., or about six pounds of acid to the barrel of oil. The acid, as drawn off, is dark-blue or reddish-brown in color, and is charged with sulpho-compounds of the hydrocarbons other than paraffins and polymerized products, while free sulphur dioxide gas is present in abun-The oil, after treatment, consists of the paraffin hydrocarbons almost freed from impurities. In color it has been changed to a very light straw shade. The oil is now washed with water introduced through a perforated pipe running around the upper circumference of the tank This water percolates through the body of the oil, removes the acid, and is allowed to escape in a constant stream from the bottom. When the wash-water shows no appreciable acid taste or reaction, the washing is stopped, and about one per cent. of a caustic soda solution of 12° B. is introduced, and the oil is again agitated. When this is drawn off, the oil is ready for the settling tanks. A washing with water after the sods treatment is sometimes followed, but it is not general. A washing with dilute ammonia is also sometimes used to remove the dissolved sulphocompounds. The settling tanks are shallow tanks, exposed to air and light on the sides, and here any water contained in the oil settles out and the oil becomes clear and brilliant. They are provided with steamcoils for gently warming the oil in cold weather to facilitate this separa. tion. A spraying of the finished oil to raise the fire-test by volatilizing a small quantity of the lighter hydrocarbon present was formerly practised at this stage, but this result is now obtained by "steam-stilling" and collecting the volatile vapors.

The Lima oil and Canadian oil, which, as before stated, contain sulphur impurity, cannot be refined and good illuminating oils obtained by this simple treatment with acid and alkali. Various methods of

treatment have been proposed and patented for these oils, such as the alternate treatment with litharge and caustic soda, distillation over finely-divided copper and iron, but the method finally adopted and now in successful use is to distil over a mixture of oxides of copper and lead, which take up the sulphur. The oil is also sold for fuel purposes. This latter utilization has been one of great importance, and it is employed in all classes of manufacturing establishments with great success and economy as a substitute for solid fuel. With the aid of injector burners, it has been found possible to use it in smelting and annealing furnaces, in all kinds of forges, in burning brick, tiles, and lime, and for raising steam with all forms of boilers. It is used in these burners in connection with either steam or compressed air.

The residuum of the original crude-oil distillation is, as was said, distilled from the "tar-stills." The first runnings, constituting from twenty to twenty-five per cent., will have a gravity of 38° B., and are returned to the crude-oil tank for redistillation, or are treated and purified as burning oil. The paraffin oil which now runs over may be caught in separate lots as it deepens in color and increases in density. or it may be all received together to be treated in the paraffin agitator with acid and purified for the separation of paraffin wax. The agitator in this case must be provided with steam-pipes, so that its contents can be kept perfectly liquid, and the charge of acid is larger, amounting to three, four, or even five per cent. The treatment includes the usual washing with water and soda, all at the proper temperature.\* After settling, the paraffin oil goes to the chill-rooms, where, by the aid of the ammonia refrigerating machines and the circulation of cooled brine, the whole mass is brought to a semi-solid condition. This is pressed between bagging by hydraulic pressure, is filter-pressed, or more generally at present is "sweated," and the refined heavy oil which drains off is collected as lubricating oil. Its gravity should be about 32° B., fire-test, 325° F., and cold test, 30° F. The press-cake may be broken up, melted, and recrystallized, and then submitted to still greater pressure at a higher temperature (70° F.) than before, when it is gotten as "refined wax." To convert it into block paraffin, it must be washed with benzine, pressed, melted, and filtered through bone-black or other filtering medium, when it is gotten perfectly colorless and solidifying to a hard, translucent block. The characters of paraffin will be referred to farther on.

The distillation of residuum is continued until the bottom of the still becomes red-hot, when yellow vapors issue from the tail-pipe, and a dense resinous product, of a light-yellow color, and nearly solid consistency, distils over. This "yellow wax" contains anthracene, chrysene, picene, and other higher pyrogenic hydrocarbons. Its use at present is to add

<sup>\*</sup>With the lubricating oils from certain crude petroleums, it is found advantageous not to wash after the acid treatment, but to treat immediately with a strong caustic lye (of 33° B.), and then to wash as a final step. This is said to prevent the emulsifying of the oil and water which sometimes takes place and greatly retards the separating out of the oil.

it to paraffin oils to increase density and lower cold test. Its chemic character will be referred to again.

The coke remaining in the tar-still at the end of the process amoun to about twelve per cent., and is largely used in the manufacture of ele tric-light carbons. Reduced oils gotten by careful driving off of the light fractions of the crude petroleum, without cracking, as stated above, a of great value as lubricants. They are generally made by vacuum di tillation and the use of superheated steam instead of direct firing. The are either brought into the market at once, without further treatmen or after a bone-black or clay filtration. This production of filtered oi is usually combined with the manufacture of vaseline. or petrolatur as it is now known in the United States Pharmacopæia. vacuum residuum as the raw material, this is melted and run on filters of fine granular well-dried bone-black. The filters are either steam-jacketed or are placed in rooms heated by steam-coils to 120° l or higher. The first runnings are colorless, and all up to a certai grade of color go to the manufacture of vaseline. Beyond that th filtrate is known as "filtered cylinder stock," and is used as a lubricar exclusively.

3. Of Ozokerite and Natural Paraffin.—The Galician ozokerit is in the main a natural paraffin, but contains some oil in mechanica admixture. Until within ten to twelve years ago it was worked exclusively for the production of paraffin, but now not more than one-thir of the annual production is so worked. The most of it is distilled yielding five per cent. of benzine, fifteen to twenty per cent. of illuminating oil, fifteen per cent. of "blue oil," and about fifty per cent of paraffin. The "blue oil" is a buttery-like mixture of heavy oils wit paraffin crystals, and corresponds to a paraffin oil as distilled from petroleum. It is run into filter-presses and pressed, first cold, and the the press-cake broken up and pressed warm to remove the adhering oil If the paraffin scale so obtained is to be worked up into block paraffin it is repeatedly treated with benzine of not over .785 specific gravity and pressed, then melted and filtered through bone-black, as befor described under petroleum paraffin.

If the ozokerite is to be worked up as a whole into the wax-lik product known as Ceresine, the operation may be conducted in one of two ways. The older method was, after a preliminary melting of the ozokerite, to free it from earthy impurities, and continuing the heatin until all water was driven out of the melted mass, to treat it with teper cent. of sulphuric acid as long as sulphurous oxide was evolved. This was followed by treatment with water and soda solution. To most thoroughly separate out the black carbonaceous matter produced by the action of the sulphuric acid, one-half to one per cent. of stearic acid added, and this then saponified with caustic soda. The soap so forme carries down all carbonaceous matter with it, and allows the ceresist to be filtered clear by using filter-paper. The product is the Yello Ceresine, much resembling beeswax. The White Ceresine, resemblin bleached beeswax, is gotten by melting the yellow ceresine by the aid of

steam, digesting it with bone-black, with frequent stirring, and filtering through paper. The newer method, more frequently followed now, is to extract the ozokerite with benzine and ligroine. The forms of apparatus devised for this purpose allow of a complete exhaustion of the ozokerite mass and a subsequent recovery of the solvent used in the extraction.

The natural paraffin that separates spontaneously from crude petroleum, and accumulates at times, as before mentioned, in pipe-lines, etc., is chiefly used as a basis for the manufacture of vaseline and similar products, being melted and filtered through bone-black, as already described.

4. OF NATURAL BITUMENS AND ASPHALTS AND OF BITUMINOUS SHALES.—The asphalt or solid bitumen from the Island of Trinidad is exported largely to the United States, where it is used in the manufacture of roofing materials and of asphalt pavements. It yields from one and three-fourths to two and a half per cent. of paraffin on distillation, and contains sulphur as an invariable constituent. Efforts made to manufacture illuminating and other oils from the asphalt have failed of practical results.

Within recent years artificial asphalts have been made by a variety of methods. As already mentioned, the California petroleums all seem to have an asphaltic instead of a paraffin base. Hence the residuum from the refining of California crude oils is manufactured into artificial asphalts. As much as eleven per cent. of artificial asphalt has been obtained in practice from Ventura County petroleum.

Again, artificial asphalts have been made by treating Lima and Oklahoma oil residuums with a current of heated air whereby a solid tenacious mass is obtained by polymerization and oxidation. Byerlite and Sarco asphalts are thus obtained.

Still another process consists of melting oil residuums with sulphur and heating until a product is obtained which becomes solid on cooling, while hydrogen sulphide is set free. An interesting production of artificial asphalt was that of Dr. W. C. Day, who distilled a mixture of fish and pine wood and then submitted the oil obtained to a second destructive distillation. The residuum left when the distillation was carried to about 425° C. solidified to a black, shining mass, which in physical properties and chemical composition strikingly resembles Utah gilsonite.

Very much more important are the industries based upon the distillation of bituminous shales. As these shales do not contain either liquid or solid hydrocarbons as such, but much more complex compounds called bitumens, the distillation is exclusively a destructive one, and the character of the distillation products becomes dependent upon the conditions of the operation, temperature being the most important consideration. The theory of destructive distillation will be entered upon at length later (see p. 385), and we will here only say that for paraffin and illuminating oil production the distillation is essentially a low-temperature one.

The material originally used in Scotland was Boghead coal, or the

Torbane Hill mineral from Bathgate, near Glasgow, which was exhausted in 1872. This yielded thirty-three per cent. of far or oily distillate and one to one and one-half per cent. of crude paraffin. At present shales are used which furnish about thirteen per cent. of tan. The material for the German paraffin production is an earthy brown coal, which, when dry, is of a light-brownish or yellowish color and crumbling character; it yields on an average 8.1 per cent. of tar and .6 per cent. of paraffin. The shales are usually distilled with some steam, which increases the amount of the tar, as well as the ammonia from the shale. The distillation may be intermittent, but in Scotland is now carried on in a continuous process by the two methods devised by Henderson and by Young & Beilby respectively, the exhausted shale being dropped from the bottom of the upright retort into a combustion-chamber beneath. As the spent shale sometimes contains as much as from twelve to fourteen per cent. of carbon, this, with the uncondensed gas of the distillation, suffices for fuel. The several products of the distillation are (1) gas, which is freed from gasolene vapors by passing through a coke tower, down which heavy oil is trickling; (2) watery or ammoniacal liquor, which is obtained to the amount of from sixty to eighty gallons per ton of shale, and yields from fourteen to eighteen pounds of sulphate of ammonia per ton worked: (3) oily liquor, or tar proper. of dark greenish color, and ranging from .865 to .880 in specific gravity, varying in amount from thirty to thirty-three gallons per ton of shale used. This is distilled in cast-iron stills holding from two hundred to two thousand gallons, for the purpose of purifying it, until only coke amounting to from five to ten per cent. of the tar is left. The mixed distillates (the paraffin magma being added to the others), according to the usage of the German paraffin-works, are stirred with two per cent. by volume of caustic soda solution in order to take up phenols and "creosote," together with other acid products; the soda washings drawn off below, and the supernatant liquid, after washing with water, is agitated with five per cent. of sulphuric acid. The refined oil is now fractionally distilled. The first fraction (specific gravity .60 to .68) is a gasolene used for carburetting illuminating gas; the second (specific gravity .68 to .76) is naphtha, used as a solvent; the third (specific gravity .81 to .82) is illuminating oil; the fourth lubricating oil (specific gravity .865 to .900). The next distillate solidifies on cooling, yielding brown crystals of hard paraffin, whose mother-liquor, removed by a filter-press, is "blue oil," whence more but soft crystals can be obtained by artificial refrigeration. The mother-liquid of these is again treated with vitriol and soda and distilled; the earlier fractions constitute heavy illuminating oil, the later lubricating oil. The percentage of solid paraffin gotten from the crude shale oil is from eleven to twelve and a half per cent. The shale oil does not yield any product corresponding to vaseline. B. Kübner, a German paraffin manufacturer, believing that the distillations of the process just described act injuriously upon the quantity and hardness of the paraffin obtained, has modified the process as follows. He treats the crude shale oil with sulphuric acid,

and, after the separation of this, distils the oil over several per cent. of slaked lime. After the crystallization of the paraffin from the distillate, it is purified by washing with shale oils and pressing. He thus avoids one distillation and obtains a larger yield of paraffin, distinctly harder in character than the usual product.

In the Scotch shale-works the distilled oil is treated first with sulphuric acid and then with caustic soda, as in the purifying of petroleum oils, and then fractionally distilled. These fractions are again treated with acid and alkali before being considered pure enough for the market. In some works (as those at Broxburn) continuous distillation is practised, so that a set of three boiler stills and two residue- or coking-stills, used together, can put through thirty-five thousand gallons of crude oil per day. The solid paraffin, by careful processes of extraction, can be brought up to twelve and a half per cent.

#### III. Products.

1. From Natural Gas.—(a) Fuel Gas.—The great value of natural gas as fuel for manufacturing and industrial purposes has only been realized in recent years, and it was rapidly introduced as a substitute for coal and coke. In Western Pennsylvania and Ohio, particularly in Pittsburg and its vicinity, for manufacturing purposes, it had for a time almost entirely displaced coal and coke, but its production has reached a maximum, and is now rapidly falling off despite the opening of new wells. That natural gas, largely made up of methane and similar hydrocarbons, is one of the best of gaseous fuels is seen from the accompanying table, prepared by a committee of the American Society of Mechanical Engineers:

Table showing Comparative Effects of Different Gas Fuels.

Heat units yielded by one cubic foot.	Number of cubic feet needed to evaporate 100 pounds of water at 212° F.
Hydrogen 183.1	293
Water gas (from coke) 153.1	351
Blast-furnace gas 51.8	1038
Carbonic oxide	313
Marsh gas 571.0	93.8

The comparison of its work with that accomplished with solid fuel, as carried out at the works of Carnegie Bros. & Co., in Pittsburg, is also given by the same committee. Using the best selected coal, and charging the furnace in such manner as to obtain the best results, the maximum with coal was nine pounds of water evaporated to the pound of coal consumed. "In making the calculations, the standard seventy-six-pound bushel of the Pittsburg district was used; six hundred and eighty-four pounds of water were evaporated per bushel, which was 60.90 per cent. of the theoretical value of the coal. When gas was burned under the same boiler, but with a different furnace, and taking a pound of gas to be equal to 23.5 cubic feet, the amount of water evaporated was found to be

- 20.31 pounds, or 83.40 per cent. of the theoretical heat-units were utilized."
- (b) Gasolene.—The production of a light gasolene from "casing-head gas" has already been alluded to. It is now produced in Pennsylvania, West Virginia, Ohio, and especially in California, where the gas from deep wells is specially adapted to yield a considerable fraction. The product is a very light gasolene (of 85° to 95°. B.), and is usually blended with a heavier naphtha to yield a commercial product.
- (c) Lamp-black.—The burning of natural gas so as to cause separation of carbon, which is then collected as lamp-black, has been referred to. The lamp-black so manufactured has been shown to be of great purity. It is miscible with water, does not color ether, and is free from oily matter. A sample of it analyzed by Professor J. W. Mallet, of the University of Virginia, gave the following results: Specific gravity at 17° C., after complete exhaustion of air, 1.729. The percentage of composition was as follows:

Carbon	. 95.057
Hydrogen	
Nitrogen	. 0.776
Carbon monoxide	. 1.378
Carbon dioxide	
Water	
Ash (Fe <sub>2</sub> O <sub>3</sub> and CuO)	. 0.056
	99.940

- (d) Electric-light Carbons.—Still another use for carbon from natural gas is the manufacture of carbons for electric arc-lights, the purity of the material making a very pure and uniform carbon pencil possible.
- 2. From Petroleum.—The names of commercial products obtained from petroleum have, of course, been almost infinitely varied, as each manufacturer has his trade names for his special products. We shall only designate the generally-accepted classes of products. Beginning with the lightest, we have:

Cymogene, gaseous at ordinary temperatures, but liquefiable by cold or pressure. Boiling-point, 0° C. (32° F.). Specific gravity, 110° B. Used in the manufacture of artificial ice.

Rhigolene, condensable by the use of ice and salt. Boiling-point, 18.3° C. (65° F.). Specific gravity, 0.60° or 100° B. Used as an anæsthetic for medical purposes.

Petroleum Ether (Sherwood oil).—Boiling-point, 40° to 70° C. Specific gravity, .650 to .660, or 85° to 80° B. Used as a solvent for caoutchouc and fatty oils, and for carburetting air in gas-machines.

Gasolene (canadol).—Boiling-point, 70° to 80° C. Specific gravity, .660 to .690, or 80° to 75° B. Used in the extraction of oil from oil-seeds, of grease from raw wool, and in carburetting coal-gas.

Naphtha (Danforth's oil).—Boiling-point, 80° to 100° C. Specific gravity, .690 to .700, or 76° to 70° B. Used for burning in vapor-stoves

and street-lamps, as a solvent for resins in making varnishes and in the manufacture of oil-cloths.

Ligroine.—Boiling-point, 80° to 120° C. Specific gravity, .710 to .730, or 67° to 62° B. For solvent purposes in pharmacy, for burning in sponge-lamps, and in extracting fat from bones.

Benzine (deodorized).—Boiling-point, 120° to 150° C. Specific gravity, .730 to .750, or 62° to 57° B. Used as a substitute for turpentine, for cleaning printers' type, and for dyers', scourers', and painters' use.

The three grades last mentioned are sometimes mixed and under the commercial names of "gasolene" or "naphtha" used for the small motors in naphtha launches and motor boats and in automobiles.

The official "benzinum" of the U.S. Pharmacopæia has a specific gravity of 0.638 to 0.660 at 25° C., and boils between 45° and 60° C.

Burning Oil, or Kerosene.—The different burning oils are known often by special names, of which the number is legion, but they are graded by the American petroleum exporters chiefly according to the standards of color and fire-test. The colors range from pale-yellow (standard white) to straw (prime-white) and colorless (water-white). The fire-tests (see p. 40), to which the commercial oils are mostly brought, are 110° F., 120° F., and 150° F.; that of 110° going mainly to the continent of Europe and to China and Japan, and that of 120° to England. An oil of 150° F., fire-test, and water-white in color, is known in the trade as "headlight oil." An oil of 300° F., fire-test, and specific gravity .829, is known as "mineral sperm," or "mineral colza oil." "Pyronaphtha" is a product from Russian petroleum, somewhat similar to mineral sperm oil. It has a specific gravity of .865, and fire-test of 265° F.

Lubricating oils from petroleum have assumed an importance which is increasing every year. Some crude petroleums, like those of Franklin and Smith's Ferry, Pa.; Mecca, Ohio; Volcano, W. Va., and other localities, are natural lubricating oils, requiring little or no treatment to fit them for use. The other petroleum lubricating oils are gotten in one of two ways. Either by driving off the light hydrocarbons from the crude oil, yielding what is called a "reduced oil" (see p. 27), or they are the oils gotten by distilling the petroleum residuums in tar-stills.

The lightest of the lubricating oils, varying in gravity from 32° B. to 38° B., are frequently called "neutral oils." They are largely used for the purpose of mixing with animal or vegetable oils, and it is therefore necessary that they should be thoroughly deodorized, decolorized, and deprived of the blue fluorescence or "bloom" characteristic of petroleum distillates that contain paraffin. The first two results are accomplished by bone-black or clay filtration, the last in various ways, such as treatment with nitric acid, addition of small quantities of nitronaphthalenes, etc.

Heavier lubricating oils are called "spindle" and "cylinder" oils. The most important characters to be possessed by these oils are high firetest, low cold-test, and a high viscosity. (See analytical tests, p. 36.)

In the matter of lubricating oils the Russian products are, it is now admitted, distinctly superior in most respects to the American. This is because of the entire difference in the chemical composition of the two, the hydrocarbons characteristic of the Russian oil being heavier and showing less tendency to solidify at low temperatures than those of the American oils. The following statement from Boverton Redwood will illustrate this:

	Viscosity at 70° F.	Viscosity at 120° F.	Loss in viscosity, per cent.
Russian oil (sp. gr913)	. 1400	166	88
American oil (sp. gr914)	. 231	66	71
Russian oil (sp. gr907)	. 649	135	79
American oil (sp. gr907)	. 171	58	66
Russian oil (sp. gr898)	. 173	56	67
American oil (sp. gr891)	. 81	40	50
Refined rape oil (for comparison)	. 321	112	65

It is true that the disproportion is chiefly at lower temperatures, the Russian oil losing its body relatively faster than the less viscous American oil.

Gas Oils.—Since the development in recent years of the Texas oil production on a large scale, as the yield of burning oil fraction is small, much of a product known as "gas oil" (because of its use for the production of a rich oil gas by destructive distillation) has been made. This is a fraction intermediate between the burning oils and lubricating oil, relatively thin and boiling between 200° C. and 300° C.

Paraffin differs somewhat in its hardness and melting point according to the source from which it is derived. The petroleum paraffin is manufactured generally in three qualities, fusing at 125° F. (51.6° C.), 128° F. (53.3° C.), and 135° F. (57.3° C.), respectively; paraffin from shales melts at 56° C., while that from Rangoon tar melts at 61° C. and that from ozokerite at 62° C. The harder varieties are bluish-white, translucent, and glassy on the surface, while the softer varieties are alabasterwhite, dull in lustre and only translucent when heated. The harder varieties are resonant. Paraffin is readily soluble in ether, benzine, and all light hydrocarbons, ethereal and fatty oils and carbon disulphide, not entirely in absolute alcohol; while ordinary alcohol only takes up 3.5 per cent. of it. It mixes with stearine, spermaceti, and wax in all proportions. Exposed for some time under a slight pressure to a temperature below its melting point, paraffin wax undergoes a molecular change and becomes transparent; but upon a change of temperature, or upon being struck, the original translucent appearance returns.

The official "paraffinum" of the U. S. Pharmacopæia is stated to have a specific gravity of 0.890 to 0.905 at 25° C., and melts at from 51.6° C. (125° F.) to 57.2° C. (135° F.).

The harder variety of paraffin is used chiefly in candle-making, for which purpose, however, a small proportion (five per cent.) of stearic acid must be added to it to prevent the softening and bending of the candle. It is also used for finishing calicoes and woven goods, to the surface of which it imparts lustre. The softer varieties are used for mixing with wax and stearic acid in candle-making, for the preparation of translucent and water-proof paper of all grades, for impregnating Swedish matches, for the adulteration of "chewing gums," and, in recent years, for "enfleurage" or extracting delicate perfumes from flowers.

Vaseline.—This product (petrolatum of the United States Pharmacopæia and unquentum paraffini of the German Pharmacopæia) may be obtained from several of the raw materials already mentioned. In the United States, as the name petrolatum indicates, it is a petroleum product and may be called "natural vaseline," as it is merely a purified preparation of naturally existing petroleum constituents: in Germany, and elsewhere in Europe, it is either extracted from other sources (pomade ozokerine), or, as the name unquentum paraffini indicates, it is an "artificial vaseline" made by the solution of paraffin in paraffin American vaseline, as made by the Chesebrough Company and others, is gotten by taking a vacuum residuum (see p. 27) and, without any treatment with sulphuric acid or other chemicals, simply filtering it through heated bone-black. In this way the amorphous character of the hydrocarbons is not changed and no crystalline paraffin is produced, as would be the case if it were a distillation product, and, moreover, no traces of sulphonic acids can remain from the acid treatment to interfere with its use as a basis of medicinal ointments. The petrolatum of the United States Pharmacopoeia is an unctuous mass varying in color from yellowish to light amber. It is transparent in thin layers and is completely amorphous. It has a specific gravity at 60° C. (140° F.) of from 0.820 to 0.850. It melts at from 45° to 48° C. (113° to 118.4° F.).

Petrolatum liquidum of the U. S. Pharmacopæia is a colorless yellowish oily liquid of specific gravity 0.870 to 0.940 at 25° C.

The German vaseline, or unquentum paraffini, is made by taking one part of ceresine (paraffinum solidum) and dissolving it in three parts of a paraffin shale oil, known as "vaseline oil" (paraffinum liquidum). This artificial vaseline, as Engler and Böhm have shown,\* easily becomes granular on chilling, and shows its composite nature moreover by readily separating on distillation into ceresine and oil. The natural vaseline has greater homogeneity and is more viscous, although at high temperatures it seems to absorb more oxygen than the artificial preparation. At temperatures not exceeding 30° C. the oxygen absorption seems to be practically nothing in either case.

Vaseline is largely used in pharmacy and medical practice as a basis of ointments and pomades.

Crude Fuel Oil.—Much of the California and Texas oil which is of inferior value for refining is burned as fuel with suitable forms of burners. The calorific value of such crude petroleums is quite high. Poole (Calorific Powers of Fuels, 2nd edition, pp. 251 and 252) gives the following values: Pennsylvania crude 20736 B. T. U., Lima, Ohio, crude 21600 B. T. U., Petrolia, Canada, crude 20530 B. T. U., Baku,

<sup>\*</sup> Dingler, Polytech. Journal, 262, p. 468.

Russia, 20160 B. T. U., Residuum, Balacheny 21060 B. T. U., Galician oil 18416 B. T. U.

- 3. From Ozokerite and Natural Paraffin. The character of several of the products now obtained from Galician ozokerite, viz., illuminating and lubricating oils and paraffin, has been sufficiently described under other heads. The peculiar product known as Ceresine, gotten from ozokerite without distillation, remains to be described. It resembles beeswax very greatly in appearance, but is of lower specific gravity, ranging from .915 to .925, while wax is from .963 to .969. The fusing point of ceresine varies from 68° C. to 80° C. Ceresine, with a fusing point of over 75° C., shows a fracture and structure like that of wax. Its behavior to water, alcohol, ether, chloroform, fatty and ethereal oils is exactly like that of paraffin. Ceresine is extensively used as a substitute for wax as well as for most of the uses before given for paraffin. It is commended especially for the formation of matrices for galvanoplastic work, proving in this respect superior to gutta-percha. It is also being used instead of gutta-percha for hydrofluoric acid bottles.
- 4. From Bitumens, Asphalts, and Bituminous Shales. The asphaltic limestones of Europe (see p. 18) furnished the earliest known technical products, and they are still worked extensively in the manufacture of a variety of useful substances. Asphaltic limestones containing from eight to twelve per cent. of bitumen when pulverized and heated furnish a powder which by compression is made to agglutinate and forms a very satisfactory surfacing for roads, etc.

Asphalt mastic is made in Europe by incorporating with the natural asphaltic limestone purified and softened bitumens like that of Trinidad in such proportion that the resulting composition, containing from fifteen to twenty per cent. of bitumen, is available for asphalt coating purposes.

Asphalt Paving Composition.—In this country, the solid asphalts like the imported Trinidad are first softened by the incorporating with them of petroleum residuums or liquid asphalts, and then mixed with quartz sand and finely powdered rock, in such proportion that the voids between the grains of sand are properly filled. This constitutes the asphalt paving surface and is spread with the aid of a binder course of coarser material upon a cement substratum.

From the crude shale oil, already described, the following products are obtained:

Shale Oil Benzine.—Specific gravity .665 to .720, boiling-point 80° to 90° C., is colorless, of ethereal odor, and slightly peppermint-like taste. It is used somewhat as a cleansing benzine, but mainly in the purifying of the shale paraffin.

Photogene (shale naphtha).—Specific gravity .720 to .810, boiling-point 145° to 150° C., has a slight ethereal odor and peppery taste. It dissolves sulphur, phosphorus, iodine, fats, resins, caoutchouc, etc. It is used somewhat for illuminating purposes and for dissolving the fat from bones and bleaching them in the preparation of artificial ivory.

Solar oil comes into the market, according to Grotowski, in two grades,

known as prima and secunda oils, one with specific gravity .825 to .830 and a boiling-point 175° to 180° C., and the other with specific gravity .830 to .835 and a boiling-point 195° to 200° C. The oils are of slight, yellowish color, and on exposure to air and light lose their free burning qualities, somewhat through the resinifying of the trace of creosote which may remain in them. The fire-test of the solar oil is generally above 100° C., and they are in general both cheap and excellent burning oils.

Paraffin Oil.—The paraffin itself has been described under a previous heading. The expressed paraffin oil is used considerably as a lubricating oil, but is of greatest importance for gas-making. The gas from this paraffin oil is especially rich in illuminating hydrocarbons and is free from the ordinary impurities of coal-gas. It is extensively manufactured in Germany, in the Hirzel and Pintsch forms of apparatus, and in England by the Pintsch, Keith, and Alexander & Patterson processes, and compressed for use in railway carriages, etc. Its characters will be referred to more especially under the heading of illuminating gases.

# IV. Analytical Tests and Methods.

- 1. For Natural Gas.—These are the methods employed for the analysis of all varieties of illuminating gas, and will be referred to under that heading. (See p. 429.)
- 2. For Crude Petroleum.—According to the rule of the New York Produce Exchange, "crude petroleum shall be understood to be pure natural oil, neither steamed nor treated, free from water, sediment, or any adulteration, of the gravity of 43° to 48° B." (0.809 to 0.786 sp. gr.). In order to determine whether the petroleum is a "pure natural oil" a sample is subjected to fractional distillation, each fraction being one-tenth of the crude oil by volume, and the density of the several distillates is determined. The regular gradation of the densities of the fractions so obtained is taken as a satisfactory indication that the oil is a natural product.

To judge of the commercial value of a crude petroleum a fractional distillation is also desirable. For this purpose Engler's system of distillation is to be recommended. He uses a distillation flask, the shape and dimensions of which in cubic centimetres are to be seen in Fig. 6. One hundred cubic centimetres of the oil are introduced into the flask by the aid of a pipette, and heat is applied. At first wire gauze is interposed between the burner and the flask, but afterwards the naked flame is employed, the heat being so regulated that from two to two and a half cubic centimetres of distillate pass over per minute. In this way fractions differing from each other in boiling-point by 50°, 25°, or 20° C. can be obtained. As soon as the requisite temperature (150° C. for the first fraction) is attained, the lamp is withdrawn until the temperature has fallen at least 20° C., when the oil is reheated to the boiling-point and again cooled, this process being repeated until no more distillate is obtained. The oil is then heated to the next boiling-point, and the cooling and reheating process repeated, and so on. In this way results can be obtained with not more than a variation of one per cent. even in the hands of different observers. In practice the fractions up to 150° C. are added together for the light naphtha or benzine, those between 150° C. and 300° C. for the burning oil, and those above 300° C. for lubricating oils and residuum.

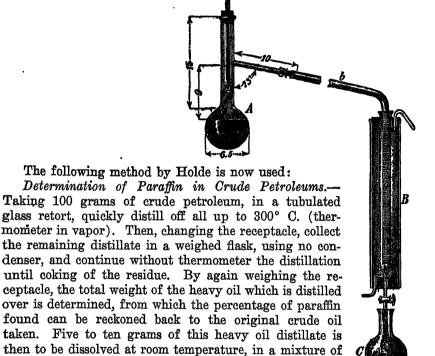


FIG. 6.

all the oily portions remain dissolved at —20°, and only paraffin flakes are visible. These latter are then to be filtered on a small filter, surrounded by a cooling mixture of ice and salt kept at a temperature of —20°, the liquid being drawn off by connecting with a suction pump, the separated paraffin on the filter being washed with previously cooled alcohol-ether mixture, until no oily portion shows in the washings. The precipitate is then taken from the ice mixture, washed off of the filter into a tared glass dish, with the aid of warm benzine, the benzine being then carefully evaporated over the water-bath. If, on cooling the dish, it is found that the paraffin is of hard variety, it is dried for fifteen minutes at 105°, and, after cooling in the desiccator, weighed. If, on the other hand, the residue is soft paraffin, melting under 45°, this is best dried by keeping it in a vacuum desiccator at a temperature of 50°,.

one part ether and one part alcohol, until clear solution is obtained. Then cooling down with the aid of an ice mixture until a temperature of —20° C. is obtained, add so much additional of the mixture of alcohol and ether, until

and then weighing. To the weighed amounts of paraffin so obtained, is to be added, because of the slight solubility of paraffin in the alcoholether mixture, .2 of one per cent. when the distillate is perfectly liquid, .4 per cent. in the case of distillates which show a separation of solid material at 15°, and one per cent. in the case of solid distillate masses.

With these corrections, the determination is regarded as accurately representing paraffin in crude oils and in lubricating oils. For such petroleums as contain both paraffin and asphalt base, the modification made by Clifford Richardson (*Jour. Soc. Chem. Ind.*, May 31, 1902) is to be used.

3. For Petroleum Products.—For commercial petroleum products, which are, of course, mixtures of hydrocarbons, the boiling-point becomes of only secondary importance, while, with reference to their uses as illuminants, the element of safety comes into consideration, so that what is called "flash point" and "burning point," together included in what is known as "fire-test," becomes important. For lubricating oils, the consistency or body determined in the viscosity-test and the "cold-test," or point to which they can be chilled without separating paraffin, is important. For paraffin and solid products the melting-point and amount of oil enclosed are important. And for all classes the color is a not unimportant gauge of purity. So that the general applicable analytical tests for petroleum products may be summed up under the following heads:

Specific gravity.

Fire-test, including flash-point and burning point.

Cold-test.

Viscosity.

Melting point.

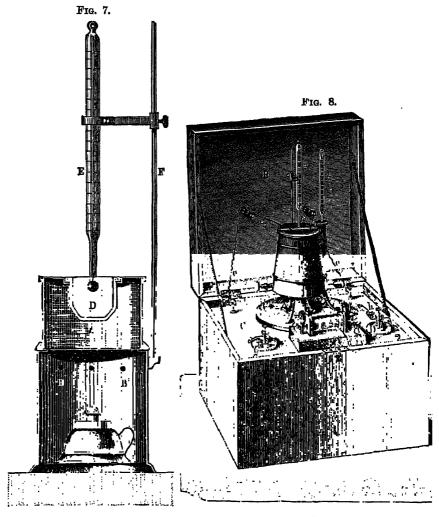
Compression-test.

Colorimetric tests.

(a) Specific Gravity Determinations.—While, of course, the methods of the specific gravity bottle and the specific gravity balance are available, the determinations are, in the case of the liquid petroleum products, almost universally made with hydrometers, and these may be of two kinds, either graduated so that specific gravities are read off direct in decimal fractions less than one, or graduated in the arbitrary scales of Beaumé, Brix, Gay-Lussac, or Twaddle, the relations of which to simple fractional specific gravity numbers are known. In America and Russia the Beaumé scale is universally adopted; in Germany, the Brix spindle is used officially by customs officers; in France, the Gay-Lussac; and in England, the Beaumé scale for liquids lighter than water, and the Twaddle for liquids heavier than water. For the formulas for conversion of readings of these scales into specific gravity figures and for a complete table of Beaumé degrees in comparison with the corresponding specific gravity figures, see Appendix. The use of direct specific gravity hydrometers is gradually extending, especially in Germany, as they do away with the necessity of all reduction tables. The specific gravity tables for liquids lighter than water are calculated for a temperature of 60° F., and in practice it is customary to add to or subtract from the observed specific gravities .004 for every 10° F. above or below 60° F. and this is found to afford a sufficiently close approximation to the truth for all commercial purposes in the case of all the ordinary petroleum products.

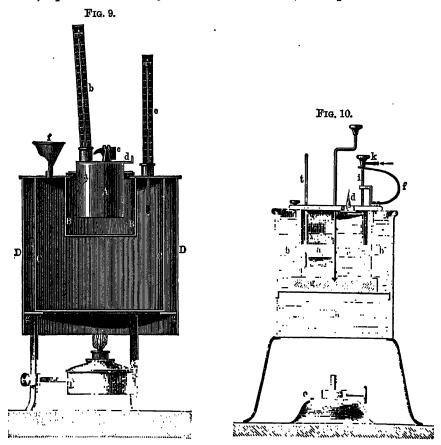
(b) Fire-test.—Just as crude petroleum is dangerous because of the dissolved gases, although its specific gravity may be relatively high, so illuminating oils may give off, at temperatures far below their boiling point, small amounts of inflammable vapors, which might make these oils dangerous for use in lamps where the oil reservoir gradually becomes warm. A distillate may have vapors of higher and lower boiling-poin carried over with it. Two points may be determined with a petroleum oil, the flashing point, or the temperature at which the oil gives of vapors which, mixing with air, cause an explosion or flash of flame dying out, however, at once, and the burning point, or the temperature at which a spark or lighted jet will ignite the liquid itself, which ther continues to burn. The latter point is usually 6° to 20° C. higher than the former, but there is no fixed relation between them. The danger of course, begins when an oil will flash, so the flash-point is generally taken as the basis of legal prescription; Austria and the New York Produce Exchange alone recognize formally the burning-test instead of the Most European countries and most of the States in the United States prescribe a flash-test. The United States have no national regulation on the subject.

The different forms of apparatus in use to determine the safety of oils are based upon either one of two principles,—the direct determination of flash or burning point, or the determination of the increased tension of vapor which the oil shows as the temperature rises. The second class is represented by a single form of apparatus, that of Salleron-Urbain used to some extent in France; the first class is represented by a dozen or more different forms, chiefly of American, English, and German inven-The earliest form, that of the Tagliabue open-cup tester, is shown in Fig. 7, in which the glass cup D, holding the oil to be tested, is heated by the water-bath A. When the thermometer, the mercury of which is just immersed, indicates 90° F. (32° C.), the spirit lamp is withdrawn and the temperature allowed to rise more slowly to 95° F. (35° C.), when a lighted splinter of wood is passed to and fro over the surface of the oil. If the gas rising from the oil does not ignite, the water-bath is heated again and tests are made when the thermometer indicates 100° F. (38° C.), 104° F. (40° C.), and 108° F. (42° C.). A flash at 108° F. is considered as marking the oil at 110° F. This form was the first one officially adopted in the United States, and is still used somewhat in Germany and Austria. The New York Produce Exchange and the American petroleum inspectors have now adopted an open-cup tester, known as the Saybolt tester, in which the electric induction-spark is made to pass over the top of the open oil-cup. It is shown in Fig. 8 F is a water-bath, the temperature of which is noted by an independent thermometer. Although this was a decided improvement on the first Tagliabue apparatus, it was found that, like the other open-cup apparatus, it gave readings which were variable and higher than if the to of the cup were covered. This led to the study of the whole subject b Sir Frederick Abel, at the request of the English government, and the adoption by the English government as their official standard of the study of the english government.



Abel tester. This has since been adopted by the German government well, and is considered by many to be the most exact now in use. It shown in Fig. 9. The following is a description of the details of tl apparatus: "The oil-cup consists of a cylindrical vessel, two inches diameter, two and two-tenths inches high (internal), with outward projecting rim five-tenths inch wide, three-eighths inch from the to and one and seven-eighths inches from the bottom of the cup. It made of gun-metal or brass (17 B. W. G.), tinned inside. A bracket

consisting of a short, stout piece of wire, bent upward, and terminating in a point, is fixed to the inside of the cup to serve as a gauge. The distance of the point from the bottom of the cup is one and a half inches. The cup is provided with a close-fitting, overlapping cover, made of brass (22 B. W. G.), which carries the thermometer and test-lamp. The latter is suspended from two supports from the side by means of trunnions, upon which it may be made to oscillate; it is provided with a



spout, the mouth of which is one-sixteenth of an inch in diameter. The socket which is to hold the thermometer is fixed at such angle, and its length is so adjusted, that the bulb of the thermometer, when inserted to full depth, shall be one and a half inches below the centre of the lid. The cover is provided with three square holes, one in the centre, five-tenths inch by four-tenths inch, and two smaller ones, three-tenths inch by two-tenths inch, close to the sides and opposite each other. These three holes may be closed and uncovered by means of a slide moving in grooves and having perforations corresponding to those on the lid. In moving the slide so as to uncover the holes, the oscillating lamp is caught by a pin fixed in the slide and tilted in such a way as to bring the end

of the spout just below the surface of the lid. Upon the slide being pushed back so as to cover the holes, the lamp returns to its origina position." Not only are all the dimensions of parts in the Abel apparatus prescribed most minutely, but the method of carrying out the tesmust be followed in minute particulars in order to get accurate result. The opening and closing of the slide must be regulated either by seconds pendulum or, as in the official German apparatus, by exact clock work. It gives a flash-test which, on the average, is 27° F. lower that that of the open-cup apparatus, so that 73° F. Abel test is taken as the equivalent of 100° F. open-cup test.

A German apparatus, which seems to be fully as exact, and simple in its construction and operation, is Heumann's tester, shown in Fig. 1 In it the results are to a considerable degree independent of the dimer sions of the oil-cup, size of flame, temperature of water, etc. This apparature ratus shows to what temperature a specimen of petroleum must k heated through and through in order that the vapor given off may suffic to make an explosive mixture with a volume of air exactly equal to th volume of oil. The glass oil-vessel, g, is set direct in the metallic water bath, b, and is exactly half-filled with oil with the aid of a measure accompanying the instrument. The agitating paddles, c, agitate the o and the air-and-vapor mixture independently. The little flame or lam for igniting the explosive mixture is attached to a button at d, and her is a small hole through which the gas-and-air mixture escapes, and, whe ignited, yields a flame about five millimetres high. In making the tes after agitation of the mixture, the button, k, is pressed down until tl little flame is pushed below the surface, when, if the temperature flashing has been reached, it ignites the explosive mixture of air ar vapor, and is blown out in turn by the slight puff of the explosion. Tl apparatus is said to give results agreeing perfectly with those gotte with the more complicated but official Abel tester. Other forms of app ratus are those of Engler (a closed test apparatus with the Saybo electric spark attachment), of Parrish, used in Holland, and of Bernstei

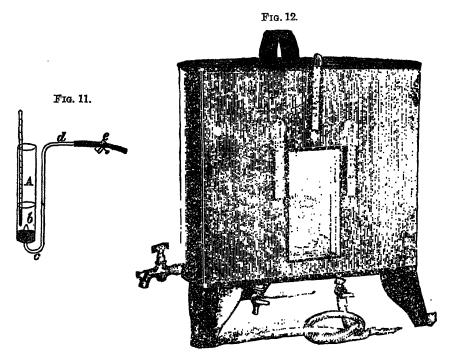
Victor Meyer first adopted the principle that the true flash-point a petroleum is that temperature at which air, shaken with petroleum can be ignited by a small flame, and proposed the thorough agitation the warmed oil to be tested with air before applying the flame. The simplest form of apparatus in which this principle is applied is the flash-tester of Stoddard, shown in Fig. 11. The air-current escapes from a fine-drawn opening in the glass tube, and must raise a foam sever millimetres in height on the surface of the oil. The cylinder containing the oil may be a small Argand lamp-chimney, and the whole apparate is lowered into a water-bath. The little jet of flame is passed to an afro over the opening at the top of the chimney, while the thermometer immersed in the oil, is read.

For lubricating oils where the flash-point is to be determined wi accuracy, the Pensky-Martens testing apparatus, which is a modific tion of the Abel tester, is used. Mechanical agitation is provided, at the oil-cup is surrounded with an air-bath. In the United States the

flash test of lubricating oils is generally taken in a shallow open cup heated directly, the temperature being raised at the rate of 8° F. per minute.

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(c) Cold Test.—This is applied chiefly to lubricating oils. The execution of it with Tagliabue's standard oil-freezer is shown in Fig. 12. The glass oil-cup, four inches in depth and three inches in diameter, is adjusted to a rocking shaft, seen at the side of the cup, so as to show by its motion whether the oil is congealing or not. Surrounding the oil-cooling chamber is the ice-chamber, and outside of this is a non-con-



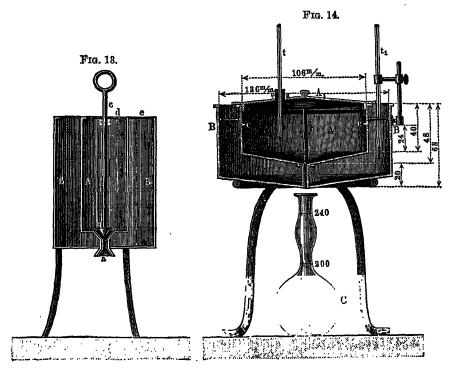
ducting jacket filled with mineral wool. Three thermometers are used: one in the oil-cup and the other two in the ice-chamber to either side. Two stopcocks below, communicating with the cooling-chamber, allow of the forcing in of warm atmospheric air to raise the temperature within when necessary. A glass door in the side opposite the oil-cup allows of the reading of the thermometer without opening the cooling-chamber. The cold-test is also frequently applied by simply taking the oil in a sample bottle, the diameter of which is about one and a half inches, chilling it in a freezing mixture, and noting the temperature at which, on inclining the tube, the oil no longer flows, or that at which the separation of paraffin commences.

(d) Viscosity Test.—As before stated, the "viscosity" or body of a lubricating oil is one of its most important characters. Its determination is, therefore, to be made with great care. The earlier forms of apparatus consisted simply of glass tubes, of pipette form, which, being

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filled with oil to a certain mark, were allowed to empty while the time was accurately noted. The pipette was set in a hot-water funnel or similar vessel, and the water in this outer vessel brought to 60° F., so that the observation on the oil might be at a standard temperature.

Other forms are those of Coleman, Mason, and Redwood, in England, and F. Fischer and C. Engler, in Germany. The Redwood viscosimeter, a very accurate instrument, will be found described and illustrated fully in "Allen's Commercial Organic Analysis" (2d ed., vol. ii. p. 198). The Fischer viscosimeter is shown in Fig. 13. The outer vessel, B.



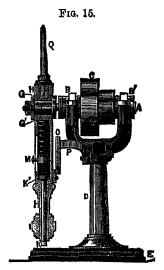
having been filled with warm water, the oil-vessel, A, has placed in it about sixty-five cubic centimetres of the oil sample, filling it to a mark on the inside. When the thermometer, immersed in the oil, shows the proper temperature, fifty cubic centimetres are allowed to run into a graduated flask placed below and the time required for its flow noted. The exit-tube, a, consists of a platinum tube 1.2 millimetres wide and 5 millimetres long, which is surrounded by a wider copper tube. This exit-tube is enlarged conically at either end, above to allow of the closing by the conical plug, b, and below to allow of the better flow of the escaping oil. In the Engler instrument, illustrated in Fig. 14, still greater care is taken to insure accurate measurement of the volume of oil operated upon, and that it shall flow under exactly similar conditions in comparative tests. Two hundred and forty cubic centimetres of water fill the inner vessel just to the mark c, and when the temperature

of 20° C. (68° F.) is reached, two hundred cubic centimetres are ru out into the vessel below. The oil to be tested is similarly filled in t the mark, and when the temperature 20° C. is reached, after keeping th oil at this for some three minutes, the plug, b, is withdrawn, and tw hundred cubic centimetres are run into the vessel below, while the tim required is accurately noted. This time in seconds, divided by the tim in seconds required for the running of the same volume of water, give the specific viscosity or viscosity-grade, as Engler terms it.

The lubricating value of oils can be determined best by actual us upon the surfaces where friction is felt, and instruments to determine such value are, therefore, based upon experimental trials of the diminution of friction on moving surfaces, when covered by the oils to be con

pared. Such an instrument is the well-known Thurston lubricating oil-tester, shown in Fig. 15, in which both the resistance in the speed of revolution of a rotating axis due to friction and the heating of the axis and the bearing in which it rotates are measured.

Mineral lubricating oils are frequently adulterated with seed oils like "blown rape oil" or blown cottonseed, both being added to give increased viscosity. Artificial viscosity is also given to less viscous mineral lubricating oils by the addition of aluminum oleate or palmitate. These fixed oils may be detected by saponifying with alcoholic potash (see p. 88). For the detection of rosin oil adulteration Allen recommends the addition to a few drops of



the sample dissolved in about one cubic centimetre of carbon disulphic of a solution of stannic bromide with excess of bromine in carbon disuphide. (The stannic bromide is prepared by allowing bromine to fadrop by drop upon granulated tin contained in a flask immersed cold water.) The production of a fine violet color indicates the present of rosin oil. Gumming tests for lubricating oils are now considered important, as oils containing much dissolved pitchy or asphaltic matteresinify rapidly at 50° C. to 100° C., while pure hydrocarbon lubricating oils slowly evaporates without resinification.

Determination of Asphaltic Residue in Lubricating Oils.—Hold gives the following method. Five grams of the oil are dissolved at 1st C. in 25 volumes of ether; to this solution is added from a burette drown by drop with constant shaking of the mixture 12.5 volumes of alcoholof ninety-six per cent. strength. After allowing the mixture to stand for five hours at 15°, it is filtered through a folded filter, washed with mixture of alcohol-ether (1:2) until no further oily substances by traces only of pitchy constituents go through into the filtrate. The washe asphaltic residue, which can also contain paraffin, is dissolved in benze

the solution evaporated to dryness, and the residue extracted by thirty cubic centimetres of ninety-six per cent. alcohol at boiling temperature, repeated again until the extraction liquor on cooling shows no further precipitation of paraffin. The residue is then dried for a quarter of an hour at 105° C. and weighed when cold.

- (e) Melting Point.—The "melting point" of paraffin should rather be called the congealing point, as what is taken usually is the temperature at which the sample, after having been melted, and while in the The American test is conprocess of cooling, begins to solidify. ducted by melting sufficient of the samples to three-fourths fill a hemispherical dish three and three-fourths inches in diameter. A thermometer with a round bulb is suspended in the fluid so that the bulb is only three-fourths immersed, and the material being allowed to cool slowly, the temperature is noted at which the first indication of filming, extending from the sides of the vessel to the thermometer bulb, occurs. English test is made by melting the sample in a test-tube about threequarters of an inch in diameter, and stirring it with a thermometer as it cools, until a temperature is reached at which the crystallization of the material produces enough heat to arrest the cooling, and the mercury remains stationary for a short time. The results afforded by this test are usually from 21/2° to 3° F. lower than those furnished by the American test. The melting point is also sometimes determined by observing the temperature at which a minute quantity of the sample previously fused into a capillary tube, and allowed to set, becomes transparent when the tube is slowly warmed in a beaker of water.
- (f) Compression Test.—Paraffin scale usually contains oil and sometimes water. The percentage of oil is determined by subjecting a weighed quantity of the material to a given pressure for a specified time and noting the loss in weight. The test is made at 60° F., the quantity of material employed five hundred grains, the pressure is nine tons over the whole surface of the circular press-cake, five and five-eighths inches in diameter, and this pressure is maintained for five minutes, the oil expressed being absorbed by blotting-paper.
- (g) Colorimetric Test.—The color of petroleum oil is determined in the United States (as regards oil for export), in England, and in Russia (in the case of oil for export) mainly by the use of the Wilson chromometer. In Germany they use both a modification under the name of the Wilson-Ludolph chromometer and Stammer's colorimeter. The Wilson instrument, shown in Fig. 16 and Fig. 17, is fitted with two parallel tubes, furnished with glass caps, and at the lower end of the tubes is a small mirror by means of which light can be reflected upward through the tubes with an eye-piece. One of these tubes is completely filled with the oil to be tested, and beneath the other tube, which remains empty, is placed a disk of stained glass of standard color. On adjusting the mirror and looking into the eye-piece the circular field is seen to be divided down the centre, each half being colored to an extent corresponding with the tint of the oil and of the glass standard respectively. An accurate comparison of the two colors can thus be made. The glass

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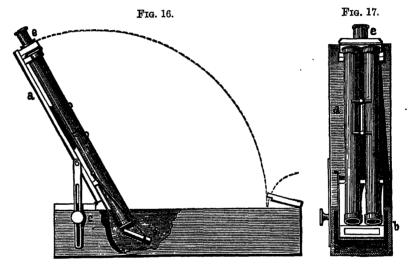
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disks, which for the English trade are of five shades of color, terms good merchantable, standard white, prime white, superfine white, an water white, are issued by the Petroleum Association of London. I Germany, the Bremen Exchange recognizes seven shades of color, straw, light straw, prime light straw to standard white, prime light straw to white, standard white, prime white, and water white.

In addition to these special tests there may be mentioned a gener method recently devised by A. Riche and G. Halphen (*Journ. Pharr Chem.*, 1894, xxx. 289) for determining whether a petroleum distillar has been obtained from American or Russian crude petroleum, and for distinguishing crude petroleum from mixtures of petroleum distillar and residuum. The process consists in the gradual addition by mean



of a burette of a mixture of equal volumes of anhydrous chloroform ar ninety-three per cent. alcohol to four grammes of the sample of the cuntil solution is effected and the liquid becomes clear. It was four that samples of crude petroleum required much more of the solvent produce a clear liquid than fractions of the same density obtained I distillation, and that the higher boiling fractions of American petr leum required a larger quantity of the solvent than sufficed for the Russian product of corresponding specific gravity.

4. For Ozokerite.—The physical tests are the same as those for paraffin scale.

5. For Asphalts.—When asphalts and bitumens are to be used for varnish-making, the determination of the total bitumen soluble in carbor disulphide or oil of turpentine suffices. When, on the other hand, the asphalt is to be considered with reference to its value for asphalt paving purposes, it is necessary to examine into the quality of the bitume For this purpose the total bitumen (amount soluble in carbon distiphide), organic non-bitumen, and ash are first determined. Then the amount of bitumen soluble in petroleum-naphtha (so called petroleum)

is ascertained. The difference between this and the total bitumen called asphaltene. The former of these portions is in general tough as elastic. while the latter is hard and brittle. For paving purposes t asphalt should contain an excess of petrolene over asphaltene.

Clifford Richardson considers it desirable to extract with naphth of 62° B. and 88° B. separately, in order to get a correct estimate the quality of the "petrolene." Chloroform is also used at times place of carbon disulphide.

The liquid asphalts or malthas sometimes contain so much materi volatile at temperatures below 300° F. that the simple determination bitumen soluble in petroleum-naphtha would be misleading and valuele unless they were previously heated to drive off these light oils, as the volatile portions are not comparable in value with the petrolene of sol asphalts. Therefore a test is commonly made of the percentage of lc in such asphalts when heated to 300° F. or 400° F. for ten hours, as this is then taken in connection with the extraction tests.

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### STATISTICS.

1. FOR NATURAL GAS.—The production of natural gas is not official reported in quantities, but in value based on the coal displaced as fuel.

Approximate Value of Natural Gas produced in the United States, 1904-09.

Localities.	1904.	1907.	1908.	1909.
Pennsylvania Ohio Indiana West Virginia Kansas Other States	\$18,139,914 5,315,564 4,342,409 8,114,249 1,517,643 1,066,981	\$18,554,245 7,145.809 1,750,715 13,785,343 4,010,986 1,672,834	\$19,104,944 8,244,835 1,312,507 14,837,130 7,691,587 3,616,803	\$20,475.207 9,966,938 1,616,903 17,538,565 8,293,846 5,485,482
Total	\$38,496,760	\$46,873,932	<b>\$</b> 54,807,306	\$63,376,941

Canada, also, in 1910 produced natural gas to the value of \$1,312 614.

2. For Petroleum.—The most important petroleum-producing cou tries for the years 1907-1910 furnished the following amounts of petr leum, expressed in metric tons and percentage proportion:

	1907.	1908.	1909.	1910.
United States Russia Dutch Indies Galicia Roumania British Indies Other countries	Per cent. 22,149,862—63,12 8,247,795—23,50 1,178,797— 3,86 1,175,974— 3,86 1,129,097— 3,22 579,316— 1,65 633,245— 0,79 85,094,086 100.00	Per cent, 24,401,728—62,97 7,554,600—19,75 2,348,000— 6,06 1,754,002— 4,53 1,147,727—2,96 568,000— 1,46 880,000— 2,27 38,754,057 100.00	Per cent, 24,433,528—62,33 8,087,300—20,50 1,497,275— 3,82 2,150,000— 5,49 1,263,946—3,22 905,338— 2,31 910,000— 2,33 39,197,385 100,00	29.585,973—64.68 8.952,793—19.57 2.024,000—4.42 1,491,600—3.26 1,352,300—2.95 1,017,000—2.22 1,328,880—2.90 45,752,546 100.00

The production of the United States for the years 1906 to 1910 was distributed as follows (in barrels of 42 gallons):

	1906.	1907.	1908.	1909.	1910.
California Colorado Gulf {Texas Gulf {Louislana Lima {Indiana Lima { Ohio Bullinois Mid-Continental { Kansas Mid-Continental { Oklahoma Kentucky and Tennessee Appalachian { New York West Virginia Other States	80,588,000 400,000 13,000,000 } 7,000,000 } 25,680,000  21,924,905 1,200,000 27,345,600 8,000 3,000	39,748,375 381,851 17,322,917 17,385,485 24,281,978 45,938,649 820,844 20,356,902 9,339 4,000	44,854,737 17,318,330 10,032,305 38,685,106 48,323,810 	54,433,010 11,912,058 8,211,448 30,898,339 49,804,922 	77,707,54 15,894,25 6,600,00 38,000,00 58,429,31 26,550,00
	127,099,505	166,095,885	179,572,479	182,134,274	213,531,11

(The Mineral Industry for 1910 and U. S. Geol. Survey, 1907.)

The exportation of crude oil and the various products therefrom for the years 1903-1907 is shown in the annexed table:

Year ending June 30th.	Mineral crude (all gravities).		Naphthas, benzine, gasolene, etc.		Illuminating oils.		
1903 1904 1905 1906 1907	Gallons. 134,892,170 114,576,920 123,059,010 139,688,615 128,175,787	Dollars. 6,329,899 6,572,923 6,359,435 7,016,131 6,626,896	Gallons. 13,139,228 16,910,121 30,816,655 32,756,694 26,357,054	Dollars. 1,225,661 1,802,207 2,575,851 2,613,677 2,735,598	Gallons. 699,807,201 741,567,086 882,881,953 864,361,210 894,529,432	Dollars. 47,078,971 57,902,503 56,169,606 54,181,617 56,249,991	
Year ending June 30th.	Lubricating and heavy paraffin oils, etc.		Residuum and tar, pitch, etc.		Total.		
1903 1904	Gallons. 93,318,257 88,810,130 97,357,196 146,110,702 136,140,226	Dollars. 12,052,927 12,048,842 13,142,860 17,974,721 17,179,562	Gallons. 22,801,506 22,560,510 48,949,362 75,031,824 65,228,009	Dollars. 566,115 733,994 1,545,470 2,255,181 2,063,668	Gallons. 963,958,362 984,424,767 1,123,064,176 1,257,949,042 1,250,430,458	Dollars. 67,253,573 79,060,469 79,793,222 84,041,327 84,855,715	

## BIBLIOGRAPHY AND STATISTICS.

The exportations of paraffin and paraffin wax for the same year 1903–1907, according to the same authority, were as follows:

For	1903	 201,325,210	pounds,	valued	at \$9,411,294
"	1904	 188,651,119	"	"	8,859,964
"	1905	 161,894,918	"	66	7,789,160
"	1906	 178,385,368	"	**	8,808,245
"	1907	 185.511.773	68	"	9.030.992

Next in importance to the production of the United States is that Russia. This has declined in recent years because of disturbing cause but is slowly increasing again. The figures for 1903–1907 as quot from the U. S. Geological Survey Reports are:

		Baku.	Grozny.	Total.
1903	in barrels	 71,618,386	3,972,870	75,591,256
1904	" "	 73,723,290	4,813,365	78,536,655
1905	" "	 49,791,356	5,168,914	54,960,270
1906	" "	 53,723,889	4,606,675	58,897,311
1907	***	 57,143,097	4,707,637	61,850,734

The petroleum consumption of different countries in kilos. for the year 1904, reckoned on a per capita basis, has been stated as follows:

	Population.	Consur	nption	in 1904.	Per ca consum	pit: pti
United States of America	80,000,000	20,166,803 n	netri <b>c</b>	centners	25.21 k	cilc
Germany	58,000,000	7,990,601	"	"	13.78	"
England	44,000,000	5,209,330	"	"	11.84	"
France	38,000,000	3,122,097	"	"	8.22	"
Russia	140,000,000	10,507,887	"	"	7.51	"
Japan	45,000,000	2,993,700	"	"	6.65	"
Roumania	6,000,000	270,247	"	"	4.50	"
Austria-Hungary	50,000,000	2,155,464	"	"	4.32	"
India	300,000,000	5,089,290	"	"	1.70	"
China	300,000,000	2,544,645	"	"	0.85	"

3. FOR ASPHALT AND SHALE OIL INDUSTRY.—The production asphalt and bituminous rock in the United States in recent years here, according to "Mineral Resources of the United States for 1909"

	Short tons.	Value.
1906	96,532	\$1,019,102
1907	154,906	2,103,698
1908	122,156	1,572,616

The importations of asphaltum of various kinds, according to "Mineral Resources of the United States for 1909," have been:

	Short tons.	Value.
1908	147,685	\$587,698
1909	148,744	646,655

## 52 PETROLEUM, MINERAL OIL, AND ASPHALT INDUSTRY.

The estimated quantity of bituminous shale distilled in recent years in Scotland, according to Boverton Redwood ("Petroleum and its Products," 2d ed., vol. i, p. 419), was:

1890	2,180,483	tons.	1900	 2,282,221	tons.
1891	2,337,932	æ	1901	 2,354,356	66
1892	2,077,076	cc .	1902	 2,107,534	66

The following are the figures for the German mineral-oil trade for 1892–93. Forty-eight shale-oil works were operated with 1297 ovens and 1067 workmen; 20,521,453 hectolitres of coal were distilled, and 1,195,892 centners of tar and 5,651,566 centners of coke were obtained. The tar was valued at 4,345,422 marks and the coke at 1,643,748 marks. On working up the tar there were obtained 159,250 centners of hard and soft paraffin, 102,306 centners of solar oil, and 623,691 centners of different paraffin oils. The value of the combined products was 11,098,496 marks.

## CHAPTER II.

#### INDUSTRY OF THE FATS AND FATTY OILS.

## I. Raw Materials.

- 1. OCCURRENCE OF THE MATERIALS.—The fats and fatty oils are of . both vegetable and animal origin. They occur not only widely spread through these two kingdoms of nature, but constitute often the larger proportion by weight of the material in which they are found. No part of the plant seems to be entirely wanting in fat, although that found in the leaves is more of a wax-like character than the oil obtained from the seeds and fruit; in the animal, fats are present in all tissues and organs and in all fluids with the exception of the normal urine. plants the percentage of fat seems to be in inverse ratio to the percentage of starch and sugar, and ranges from sixty-seven per cent. in the Brazil nut to one per cent. in barley. While the oil-bearing plants are far too numerous to allow of a complete enumeration here, it will be desirable to state first the occurrence of those technically most important, and afterwards to examine those physical and chemical differences which lie at the basis of their different uses. Similarly the most important animal oils and fats will first be enumerated.
- (a) Vegetable Oils, Fats, and Waxes.—Castor oil (oleum ricini, ricinus-oel) is extracted by pressure or heat from the seeds of the Ricinus communis, originally from the East. It is a thick oil, of specific gravity .9669 at 15° C., colorless or yellowish, transparent, of mild taste, but becoming rancid on long exposure to air, miscible with alcohol and ether, and easily saponifiable. The shelled seeds yield from forty to fifty per cent. of the oil.

Cotton-seed oil (oleum gossypii seminum, baumwollen-samen-oel) is obtained by pressure from the hulled seeds of the several species of Gossypium, or cotton-plant. The raw oil is brownish-red in color, somewhat viscid, of specific gravity .920 to .930 at 15° C., and separates some palmitin at from 6° C. to 12° C. The refined oil has a strawyellow color, or is colorless, of pleasant nutty flavor; specific gravity, .9264 at 15° C.; boils at about 600° F., and congeals at about 50° F. for summer- and 32° F. for winter-pressed. Even at the ordinary temperature, cotton-seed oil deposits "stearine" on standing. The finer brands of cotton-seed oil intended for edible and culinary purposes are freed from this "stearine" by chilling or simply by allowing the oil to stand for some time in large storage tanks. It possesses slight drying properties, and is saponifiable, but is chiefly used as a substitute or adulterant of lard and olive oils. The hulled seeds yield from eighteen to twenty per cent. of the crude oil.

Hemp-seed oil (oleum cannabis, hanf-oel) is obtained from the seeds of the Cannabis sativa, or common hemp. It has a mild odor but a mawkish taste, and greenish-yellow color turning brown with

specific gravity at 15° C. is .9276. It is freely soluble in boiling alcohol. Has weaker drying properties than linseed oil, but is used in paint and varnish manufacture and in making soft soaps. The seeds contain some thirty per cent. of the oil.

Linseed oil (oleum lini, lein-oel) is pressed from the seeds of the Linum usitatissimum, or flax-plant. The oil differs in quality according to the method of its production. By cold pressure is obtained twenty to twenty-one per cent. of a pale, tasteless oil, which is used in cooking as a substitute for lard or butter in Russia and Poland. By warm pressure is obtained twenty-seven to twenty-eight per cent. of an amber-colored or dark-yellow oil. It is, when fresh, somewhat viscid, but as a drying oil it gradually absorbs oxygen and becomes thick and eventually dry and hard. The specific gravity of the fresh oil is .935 at 15° C. It is used almost exclusively in the preparation of paints, varnishes, printers' ink, and "oil-cloth." (See p. 113.)

Poppy-seed oil (oleum papaveris, mohn-oel) is obtained from the seeds of the opium poppy by pressure, is of pale-yellow color, and slightly sweetish taste. Specific gravity, .925 at 15° C. The cold-drawn oil, the oil of the first pressing, is almost colorless, or very pale golden yellow; this is the "white poppy-seed oil" of commerce. The second quality, expressed at a higher temperature, is much inferior, and constitutes the "red poppy-seed oil" of commerce. It is used for salads, paints, soaps, and to adulterate olive and almond oils. The seeds yield from forty-seven to fifty per cent. of oil.

Walnut oil (huile de noix, wallnuss-oel) is obtained from the seeds of the common walnut-tree, Juglans regia. The fruit to be pressed should be fully ripe and kept for several months before being pressed, as the fresh seeds yield a tyrbid oil. The cold-drawn oil is very fluid, almost colorless, or of a pale yellow-greenish tint, and has a pleasant smell and agreeable nutty taste; the hot-pressed oil, on the other hand, has a greenish tint and an acrid taste and smell. Walnut oil is a very good drying oil, and at least equal if not superior in that respect to linseed oil. It is chiefly used by artists for paints, as it dries to a varnish film less liable to crack than the film of linseed-oil varnish. Moreover, the better brands of walnut oil being almost colorless, it is preferred to any other oil for white paints.

Sunflower oil (huile de soleil, sonnenblumen-oel) is obtained from the seeds of the sunflower (Helianthus annuus), and is a limpid pale-yellow oil of mild taste and pleasant smell. Specific gravity, .925 at 15° C. It belongs to the class of drying oils, but dries more slowly than linseed oil. The cold-drawn oil is also used in Russia for culinary purposes, while that expressed at a higher temperature is employed in soap-making and for the manufacture of varnishes.

Almond oil (oleum amygdalæ, mandel-oel) is the fixed oil obtained from both the sweet and the bitter almond. The former contains the more oil, but the latter is cheaper, and the residual cake can be utilized for the preparation of the essential oil of bitter almonds. The oil is odorless, agreeable to the taste, and of yellow color. Specific gravity, .919 at 15° C. It is used in pharmacy and medicine and in soon medical

Corn oil (maize oil, mais-oel) is obtained from the seeds of the mai or Indian corn, either by expressing the seed before it is employed f the manufacture of starch, or, where the corn has been fermented for t production of alcohol, by recovering it from the residue of the ferme tation vats. Prepared by the former process, it is of a pale-yellow golden-yellow color, whereas the oil obtained by the latter process reddish brown. Specific gravity, .921 to .924 at 15° C. The oil h slight drying properties only. It is used for soap-making, in the man facture of artificial rubber, for varnishes, and, when refined, as salad o

Sesamé oil (gingili oil, teel oil, sesam-oel) is obtained from the see of the Sesamum orientale and Sesamum indicum. The oil possesses yellow color, is free from odor, and has a pleasant taste. The col drawn oil is therefore considered equal to olive oil for table use. It h very slight drying properties. Specific gravity, .923 at 15° C. In addition to its use as an edible oil, the inferior grades are used in soa making and as burning oil.

Ben oil (oleum balatinum, behen-oel) is obtained by expression fro the seeds of the several species of *Moringia*. Colorless, odorless oil, n readily turning rancid. It is used by perfumers for extracting odo and for lubricating clocks and light machinery.

Cacao butter (oleum theobromatis) is obtained from seeds or nibs Theobroma cacao. Nearly white fat, with pleasant odor and tast Fuses at 86° F. (30° C.). Specific gravity, .945 to .952. It is used f cosmetics and for pharmaceutical preparations.

Cocoa-nut oil (oleum cocöis, kokos-oel) is obtained from the dripulp (copra) of the cocoa-nut by expression. An oil of the consistent of butter, fusing at 73° to 80° F. (22.7° to 26.6° C.). When fresh, white in color and of sweet taste and agreeable odor, but easily become rancid. It is easily saponified, even in the cold. It is used in the man facture of candles and padded soaps. (See p. 70.)

Colza and rape oils (oleum brassicæ, rüboel) are practically identically are extracted from the several varieties of Brassica campestr. The seeds are called cole-seed or rape-seed. The term "colza oil" generally applied to refined rape oil. The crude oils are used as lubicating oils, and are of dark, yellow-brown color. Refined and freed fro albumen and mucilage, they become bright-yellow. The specific gravi of the refined oil is .9132 at 15° C. Rape oil is used for lamps, for lubricating machinery, and for adulterating both almond and olive oil.

Olive oil (oleum olivarum, oliven-oel) is expressed from the fruit Olea Europæa. It differs greatly in quality according to the methody which it is obtained. The purest is nearly inodorous, pale-yellowith pure oily taste. Specific gravity, .918 at 15° C. Does not decorpose or become rancid easily, and congeals at 32° F. to a granular sol mass. The percentage of oil amounts to thirty-two per cent., of which twenty-one per cent. is furnished by the pericarp, and the remainder which is inferior, by the seed and woody matter of the fruit. It is use extensively as an article of food or condiment, in pharmacy, as an ill minant and lubricant, and in coap-making. The lowest grad, "tourns

oil," has a high per cent. of free fatty acids and readily emulsifies with sodium carbonate solution.

Arachis oil (peanut oil, erdnuss-oel). This oil is obtained from earth-nuts, the seeds of Arachis hypogæa. The cold-drawn oil of the first expression is nearly colorless, and has a pleasant taste resembling the flavor of kidney beans. Specific gravity, .917 at 15° C. The best qualities of the oil are used for table oil and the inferior grades for soapmaking.

Palm oil (oleum palmæ, palm-oel) is obtained from the fruit of several species of palm. The fresh palm oil has an orange-yellow tint, a sweetish taste, and an odor resembling violets. Its specific gravity is about .945. Its consistency is that of butter or lard. It ordinarily becomes rancid rapidly, and hence usually contains free acid. It is used in candle- and soap-making, and also to color and scent ointments, pomades, soap powders, etc.

Carnauba wax is obtained from the leaves of the carnauba palm, Copernicia cerifera of Brazil. Its specific gravity is .999 and its melting point 185° F. (84° C.). It is brittle and of yellowish color. It is extensively used in the manufacture of candles.

Japan wax is obtained by boiling the berries of several trees of the genus Rhus, from incisions in the stems of which flows the famous Japan lacquer varnish. It is properly a fat, as it consists almost entirely of glyceryl palmitate. Its specific gravity is .999 and melting point 120° F. (49° C.). When freshly broken, the fractured surface is almost white or slightly yellowish-green and the odor tallow-like. It is used for mixing with beeswax in the manufacture of candles and in the manufacture of wax-matches.

Myrtle wax, a solid fat obtained by pressure from the berries of myrica cerifera. Specific gravity 1.005 at 15° C.; fusing point 45° to 46° C. It is used as a substitute for beeswax and particularly in candle-making.

(b) Animal Oils, Fats, and Waxes.—Neat's-foot oil. Prepared from the feet of oxen collected from the slaughter-houses. It is a clear, yellowish oil of specific gravity .916 at 15° C. It does not congeal until below 32° F., and is not liable to become rancid. Of great value as a lubricant, and used for softening leather and grinding of metals.

Butter fat is the oily portion of the milk of mammalia, but in practice the term is restricted to that obtained from cows' milk. The pure fat constitutes from eighty-five to ninety-four per cent. of the finished butter. The pure fat has a specific gravity of .910 to .914, and its melting point varies from 85° to 92° F. For fuller account of manufactured butter, see under milk (p. 281.)

Lard and lard oil (adeps, schweine-schmalz) is the fat of the pig-melted by gentle heat and strained. The crude lard is white, granular, and of the consistency of a salve, of faint odor and sweet, fatty taste. Its specific gravity is .938 to .940 at 15° C. Exposed to the air it becomes yellowish and rancid. When pressed at 32° F., it yields sixty-two parts of colorless lard oil and thirty-eight parts of compact lard. The lard is

used in cooking, the lard oil for greasing wool, as a lubricant and an illuminant.

Tallow and tallow oil (sevum, talg). Tallow is the name given to the fat extracted from "suet," the solid fat of oxen, sheep, and other ruminants. The quality of the tallow varies according to the food of the tatle and other circumstances, dry fodder inducing the formation of hard tallow. Its melting point varies from 115° to 121° F. The besqualities are whitish, but it has in general a yellowish tint. Beef tallow contains about sixty-six per cent. of solid fat and thirty-four per cent of olein or tallow oil; mutton tallow contains about seventy per cent. of solid fat and thirty per cent. of tallow oil. The oil is used chiefly if the manufacture of soaps and the harder tallow for candle-making.

Bone fat is a whitish-yellow fat obtained by boiling bones or extraction of the same with benzin, and is used in soap-making.

Cod-liver oil (oleum jecoris ceselli, leberthran) is an oil ranging i color according to the method of its preparation from pale-straw to darl brown, and of specific gravity .923 to .924 or even .930 at 15° C. The finer qualities are used for medicinal purposes, the darker for tanners and curriers' use.

T. A. S.

7

Menhaden oil is obtained from the Alosa menhaden, a kind of he ring. Is used for soap-making and tanning, and, when pure, as a sulstitute for cod-liver oil.

Shark oil is prepared from the livers of various species of shark. is the lightest of the fixed oils, the specific gravity ranging from .865 : .876. It is used in the adulteration of cod-liver oil and for tanning.

Whale oil (train oil) is extracted from the blubber of the common or Greenland whale. Is yellow or brownish in color and of disagreeab odor. Specific gravity .920 to .931. It is used for illumination and for soap-making.

Sperm oil is procured from the deposits in the head of the sper whale. In the living animal, the solid spermaceti is held in solution the liquid sperm oil; when the liquid becomes cold the spermaceti sep rates out. The oil is very limpid, relatively free from odor, and bur well in lamps. Specific gravity, .875. It is used as a lubricant account of its low cold test and its viscosity, and as an illuminant.

Spermaceti (cetaceum, walrath) is the solid wax separated out fro the accompanying oil. It is yellowish at first, but when purified is whit brittle, and scaly. Its specific gravity is .943 at 15° C.; melting poir 43° to 49° C. It is only slightly soluble in alcohol, benzene, and petr leum-ether, but easily soluble in ether, chloroform, and carbon dist phide. It is used in the manufacture of candles and in pharmaceutic preparations.

Wool grease (woll-fett, lanolin, or adeps lanæ). Sheep's wool co tains a large amount of fatty matter of a peculiar character. It contains free fatty acids, esters of cholesterol and isocholesterol, and the fralcohols just named. When purified from fatty acids it yields lanoli which has the property of taking up large quantities of water in a semulsion and is used extensively in medicine. The esters are true wax and not glycerides.

Beeswax (cera flava, bienenwachs) is the substance of which the cells of the honey-bee are constructed. The crude melted wax is a tough, compact mass of yellow or brownish color, granular structure, faint taste, and honey-like odor. When bleached it becomes white. Specific gravity .959 to .969; melting point 62° to 64° C. It is used in making candles, ointments, and pomades.

Chinese wax (insect wax) is deposited by an insect, Coccus cerifera, upon the Chinese ash-tree. It is a white, very crystalline, and brittle wax, resembling spermaceti in appearance. Specific gravity .973 at 15° C.; fuses at 82° to 83° C. It is slightly soluble in alcohol and ether, very soluble in benzene. It is used in candle-making.

2. Physical and Chemical Characters of the Different Oils and Fats.—(a) Physical Properties.—Most of the vegetable fats are liquid at ordinary temperatures, because of the relatively high percentage of olein they contain. Cocoa-nut oil, palm oil, cacao butter, and a few others have a buttery consistence on account of the palmitin present. The fats of animals feeding on straw and hay are solid, because of the stearin present; the fats of carnivorous animals are all softer; the fat of fishes is liquid at ordinary temperatures, and somewhat differently constituted chemically. The solid waxes, both vegetable and animal, are in general differently constituted from the softer fats.

The fats and oils are almost insoluble in water (if the water contains albumen, gum, or alkaline carbonates in solution they readily form an emulsion with it on shaking); alcohol only dissolves them sparingly; ether, carbon disulphide, chloroform, benzene, turpentine oil, fusel oil, and acetone dissolve them readily.

On exposure to the air, the fats, and particularly the fatty oils, absorb oxygen. The heat developed by this oxidation at times suffices to inflame wool and cotton tissues soaked with the oil. The oils which absorb oxygen in this way become thick, and finally dry to translucent resinous masses. Such oils are called "drying oils," and are used in painting and varnish-making. (See p. 112.) The specific gravity of all the fats and oils is less than unity, although the vegetable waxes are only very slightly less.

The boiling-points of the oils and fats cannot in general be taken as distinctive, as many of them begin to decompose when distilled under ordinary pressure. Their fusing and congealing points are more important; particularly in the case of oils used as lubricants does the latter denote the different value of the oil for use at low temperatures.

(b) Chemical Composition of the Oils, Fats, and Waxes.—The fatty oils, as distinguished from the mineral oils (see p. 13) and the volatile oils (see p. 103), belong to the class of compound ethers. They are saltlike bodies, composed of characteristic acids (oleic, palmitic, and stearic), known as fatty acids, in combination with an alcohol or base. In most cases the base is the triatomic alcohol glycerine, so that the oils are said to be glycerides of the several fatty acids. Some few, known as waxes, do not contain glycerine, but a monatomic alcohol in combination with the fatty acid. Most of the animal and vegetable fats contain the three proximate constituents olein, palmitin, and stearin, the com-

binations of oleic, palmitic, and stearic acids respectively with glycerine. In the more liquid oils the olein predominates, in the more solid palmitin or stearin. The so-called "drying oils" contain a different acid—linoleic acid—in combination with glycerine. The fish oils contain a variety of the lower fatty acids and some solid unsaponifiable alcohols like cholesterin. The most satisfactory classification of the oils and fats is that of A. H. Allen,\* which is here given in abstract.

- I. Olive Oil Group.—Vegetable oleins. Vegetable non-drying oils. Lighter than Groups III, IV and V. Yield solid elaidins with nitrous acid. Includes olive, almond, earth-nut and ben oils.
- II. Rape Oil Group.—Non-drying oils from the cruciferæ. Yield pasty elaidins and have higher saponification equivalents than Group I. Includes rape seed, colza, and mustard oils.
- III. Cotton-seed Oil Group.—Intermediate between drying and non-drying oils. Undergo more or less drying on exposure. Yield little or no elaidin. Includes cotton-seed, sesame, sunflower, maize, soja-bean, hazel-nut, and beech-nut oils.
- IV. Linseed Oil Group.—Vegetable drying oils. Yield no elaidin. Of less viscosity than the non-drying oils. Includes linseed, hemp-seed, poppy-seed, niger-seed, and walnut oils.
- V. Castor Oil Group.—Medicinal oils. Very viscous and of high density. Includes castor and croton oils.
- VI. Cacao Butter Group.—Solid vegetable fats. Do not contain notable quantities of glycerides of lower fatty acids. Includes palm oil, cacao butter, nutmeg butter, and shea butter.
- VII. Cocoa-nut Oil Group.—Solid vegetable fats, in part wax-like. Several contain notable proportions of the glycerides of lower fatty acids. Includes cocoanut oil, palm-nut oil, laurel oil, Japan wax, and myrtle wax.
- VIII. Lard Oil Group.—Animal oleins. Do not dry notably on exposure, and give solid elaidins with nitrous acid. Includes neat's foot oil, bone oil, lard oil, and tallow oil.
- IX. Tallow Group.—Solid animal fats. Predominantly glycerides of palmitic and stearic acid, although butter contains lower glycerides. Includes tallow, lard, bone fat, wool fat, butter fat, oleomargarine, and manufactured stearin.
- X. Whale Oil Group.—Marine animal oils. Characterized by offensive odor and reddish-brown color when treated with caustic soda. Includes whale, porpoise, seal, menhaden, cod-liver, and shark-liver oils.
- XI. Sperm Oil Group.—Liquid waxes. These are not glycerides but ethers of monatomic alcohols. Yield solid elaidins. Includes sperm oil, bottle-nose oil, and dolphin oil.
- XII. Beeswaw Group.—Waxes proper. Are esters of higher monatomic alcohols, with higher fatty acids in free state. Includes spermaceti, beeswax, Chinese wax, and carnauba wax.
- 3. Extraction of the Raw Materials and Purification of the Same.—The method of extraction of the oils and fats is, of course, determined to a considerable degree by their physical condition. Solid fats, like tallow and lard, are obtained free from the enclosing membranes by melting the finely-chopped material and drawing off the fat in the melted state; animal oils are extracted mainly by boiling out with water; oil fruits and seeds are ground fine, and then the oil obtained by submitting the meal to pressure, either cold or with the aid of heat, or the oil is extracted by solvents like carbon disulphide and petroleum ether.

<sup>\*</sup> Commercial Organic Analysis, 4th ed., vol. ii, p. 64.

In the extraction of fats by the process of melting, three forms of procedure are followed: (1), the so-called "cracklings" process, a melting over direct fire, known, too, as the "dry melting"; (2), the melting over direct fire with the addition of dilute sulphuric acid, known as the "moist melting;" and (3), the melting by the aid of steam. In the first process, a little water is added and the tallow or other chopped fat is heated in open vessels. The mixture of fat globules and water at first gives it a milky appearance, but, as soon as the water is driven off, the cell membranes shrivel more and more together, forming the cracklings, and the fat appears as a clear, fused liquid. A constant stirring is required in order to prevent the fragments of membrane from sticking to the sides or bottom of the vessel and burning. The melted fat is drained from the cracklings by passing through metallic sieves, and cracklings afterwards pressed in suitable presses to recover the adhering fat, which forms a second quality tallow. A raw tallow yields on the average eighty to eighty-two per cent. of drained oil and ten to fifteen per cent. of cracklings; a very pure kidney fat will yield, however, ninety per cent, and over of drained fat.

In the second process, now generally followed, to one hundred kilos. of tallow, twenty kilos. of water mixed with one-half to one and one-half kilos. of concentrated sulphuric acid is added. The sulphuric acid attacks and destroys the cell-membranes rapidly when heated, and so allows of the liberation of the fat. In this process, as in the last, provision must be made for preventing the escape into the air of the unhealthy and offensive odors coming from the melting of the impure tallow. The escaping vapors are in part condensed and part burned under the kettles. In the third process, that of melting by steam, the steam may be directly introduced into the fat mass or indirectly used by the aid of coils of pipes.

The tallow rendering by steam is illustrated in the apparatus of Wilson, shown in Fig. 18. The steam enters through the perforated pipe G, under the perforated false bottom. The plate F having been shut down tight upon the opening E, the vessel is two-thirds filled with the tallow and steam applied. The pressure is allowed to rise to three and a half atmospheres (fifty-two and a half pounds per square inch) and kept at this for some ten hours. The condensed water collects under the false bottom and can be drawn off when necessary. The melted tallow is then run off from the stopcocks, PP, and the cracklings finally discharged through the opening E.

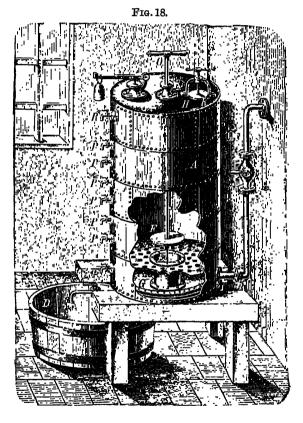
Some acid may be added to the fat or in the Evrard process, instead of acid, caustic soda, which has the advantage of combining with the noxious volatile acids evolved.

The extraction of lard takes place by similar methods to those employed for tallow, but at lower temperatures and more readily.

For the extraction of animal oils, like fish oils, the method of boiling out with water is generally employed, elevation of temperature and prolonged heating being avoided as much as possible in the case of the finer medicinal oils.

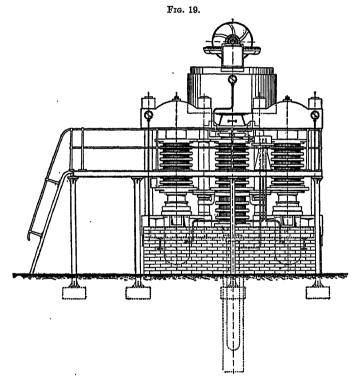
For oil-bearing fruits and seeds, the methods of obtaining oil,  $\epsilon$  already mentioned, are expression, either cold or by the aid of heat, an that of extraction by solvents.

For the expression of oils, the carefully cleaned seeds are first crushe to break the shells or kernels and then ground to fine meal. The crushing is done very generally in oil-seed mills of the type known  $\epsilon$  "edge-runners," where the two stones or metal wheels are made to revolve on a stone foundation on which the oil seeds are placed, an



from which any excess of oil may flow. A much more perfect crushir is possible in this mill than in those in which stamps are used. The are then slightly heated for the double purpose of coagulating ar plant albumen and making the oil more liquid. In the case of the be medicinal or table oils all heat is avoided and cold-pressed oils on taken. The meal is then repeatedly pressed. The result of the fir pressing is often called "virgin oil," and is of better color and tas than the later lots. The pressing is done with hydraulic presses und pressures rising to 300 atmospheres (equalling about two tons to t square inch). The crushed oil seed is placed in woolen or cotton cloth usually covered in by bags of horse-hair, and then placed between t press-plates. Following the cold pressing, or at once in the case of o

bearing seeds of lesser value, the crushed seed is warmed in a steam-jacketed kettle, which is provided with mixing appliances, and then delivered through a mixing box into bags or cloths for the hot pressing. The so-called Anglo-American open press, in which this expression is effected, is shown in Fig. 19. The other process, that of extraction of the oil by solvents, is capable of yielding a much larger amount of oil than is obtained by pressure, but has been more or less opposed on several grounds. The solvents employed are carbon disulphide and petroleumether. The former is the better solvent, is used at a lower temperature,



and is easily recovered from the solution afterwards without leaving any appreciable odor adhering to the oil. It, however, dissolves coloring matter and resin from the seed as well as oil, and so introduces impurity, and when not perfectly pure, it leaves sulphur impurities also in the oil. The other solvent does not dissolve so much coloring matter or resin, communicates no odor, and leaves no sulphur or other residues in the oil, and so can be used for fine table oils, if necessary. It requires a higher temperature, however, and, condensing on the surface of water instead of under it, like carbon disulphide, requires more complicated distillation and condensing apparatus. At the present time the carbon disulphide is more generally used. A solvent superior to either is carbon tetrachloride, which is coming into increasing use. Like carbon disulphide, it is heavier than water and insoluble in the same, but its

chief merit is its entire uninflammability. It is still rather too expesive for general use, and, like chloroform, its vapors have a certain na cotic effect. Moreover, in the presence of moisture, it attacks iron ar copper, and hence has to be used in lead-lined extraction vessels. The objection first urged against the extraction of oil by solvents, that the left the oil-cake valueless for cattle food because of the too comple extraction of the oil, is now met by the oil men, who leave eight to toper cent. of fat or oil in palm-nut or other oil-cake.

The expressed or extracted oils are in many cases in quite a cruc condition, containing both suspended and dissolved impurities of variou kinds. To purify them for use, even in soap-making, some treatment generally necessary. Often simple but prolonged subsidence suffices the impurities are only suspended. Instead of subsidence, it may I necessary at times to use filtration through cotton wadding, animal cha coal or fuller's earth. If both subsidence and filtration fail to cles the oils, it is necessary to adopt chemical treatment, as the impurities i time ferment and develop a permanent rancidity or deterioration ( the oil. The first process to note is that of Thénard, to add gradual one to two per cent. of sulphuric acid to oil previously heated to abou 100° F. and mix by thorough agitation, followed by settling and drawin off from the acid sludge. The sulphuric acid both takes up the water that holds the impurities in solution and chars the impurities themselve The treatment with acid is to be followed by a thorough washing wit warm water and final filtration. Cogan's process follows the additic of sulphuric acid by that of steam. Instead of sulphuric acid, caust alkalies are sometimes used as in the Evrard process (see p. 60), which is chiefly applied to colza and rape oils. In this case, the caustic soc saponifies a small quantity of the oil, and the soap carries down, mechan ically, all impurities, leaving the oil perfectly clear. Too prolonge agitation may, however, make an emulsion of soap and oil, which sep rates with difficulty. R. von Wagner proposed the use of zinc chloric instead of sulphuric acid, as this chars the impurities without attacking The zinc chloride is used in concentrated solution of 1.8 specific gravity, about one and one-half per cent. being taken and tho oughly agitated with the oil. After the zinc chloride solution is with drawn, the oil is well washed with water and filtered. Tannin is als used to clear some oils, which it effects by coagulating the albumen.

Cotton-seed oil is always colored by some resin, which is removed I: treatment with alkali, which saponifies the resin and the free acids of the crude oil, converting them into a mucilaginous soap which separates i dark-colored flakes when the oil is heated. This produces a light yello oil, which may be further purified by being heated to from 150° to 200 F. in kettles with fuller's earth, after which it is filter-pressed.

Still more energetic methods for purifying oils are the oxidatic methods, using "chloride of lime" or bichromate of potash, and su phuric or hydrochloric acids as applied to palm oil.

The use of hydrogen peroxide solution has recently been tried for the bleaching of oils, with the best of results. Four or five per cent. a ten per cent. solution will generally suffice if repeatedly shaken u with the oil to be treated. Sodium and calcium peroxides operate in the same way.

Ozone-carriers, like ferrous sulphate solution, will also bleach in the presence of sunlight. This method is often applied with linseed oil.

### II. Processes of Treatment.

1. Saponification of Fats.—The composition of the proximate principles, olein, palmitin, and stearin, which make up the bulk of the far proper, was first established by the researches of Chevreul in 1823. The decomposition can be effected in a number of ways, by the action of bases like the alkalies and some metallic oxides, by the action of suphuric acid liberating the fatty acids, and by the action of water alon when aided by heat and pressure.

Chevreul at first used alkalies, patenting that process in 1825, conjunction with Gay-Lussac, but this procedure was given up alread in 1831, when Ad. de Milly replaced the alkalies by lime. This was used exclusively for a number of years, but was followed in 1854 k the independent discovery of Tilghman and Berthelot of the metho of decomposing by the use of hot water superheated by high pressur Melsens also proposed the same process substantially a little later. consequence of the danger connected with the high temperature ar pressure, this process is not carried out any longer in its original shap but is now replaced by the "autoclave" process, mentioned later. ] 1841 Dubrunfaut found that if neutral fats were treated first with su phuric acid, and then boiled with water, the fatty acids might be di tilled in an atmosphere of superheated steam without decompositio This constituted the distillation process. It was extensively used in En land. Wilson and Gwynne found it possible, with proper application of the superheated steam and regulation of the temperature (290° 315° C.), to dispense with the sulphuric acid, and to decompose tl fats and then distil them without any decomposition. This process now used on a large scale by the Price Candle Company in Englan Still later, Bock, of Copenhagen, found that if the membranous cell lar tissue that enclosed the fat be decomposed by a preliminary tree ment with sulphuric acid and the charred tissue, which by oxidatic becomes heavier than the fat and sinks through it, be removed, the pu fat could be decomposed by boiling with water in open tanks. The sep rated fatty acids are so pure in color that washing suffices, and no di tillation is necessary.

These several processes have been in time modified and amalgamatuntil now only three or four processes are practically followed on a lar, scale:

- (1) The saponification by alkalies used exclusively in soap-makin and yielding a soda or potash salt of the fatty acid. (See SOAPS, p. 68
- (2) A combination of the lime and hot-water processes, known Milly's "autoclave process," in which two to four per cent. of lime

made to do the work of saponification, for which 8.7 per cent. is the oretically needed, and for which fourteen to seventeen per cent. was first used. The saponification is carried out in the presence of water strong, closed, metallic vessels, at a temperature of 172° C. One for of such vessel for the saponification by lime under pressure that has been much used is an egg-shaped cylinder. At present the form of the vess in use is more generally that of a sphere, which stands the eight to te atmospheres internal pressure better. The lime soap, technically calle "rock," after its separation is decomposed by sulphuric acid, for parts of acid to each three parts of lime used being taken. After t complete subsidence of the calcium sulphate the free fat acids are the

oughly washed with water and steam.

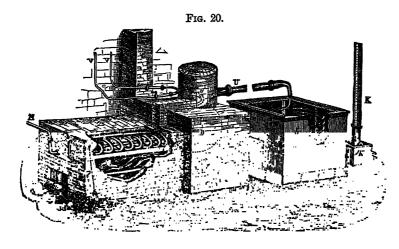
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(3) The sulphuric acid saponification, followed by distillation. process is almost exclusively followed in England. The amount of st phuric acid used has gradually been diminished, as it is found that relatively smaller percentage will suffice. For offal fats some twelper cent. is now used, for tallow nine per cent., and for palm oil s The decomposition generally requires some hours at a ter perature varying from 120° to 170° C. Milly modified this process I using a smaller quantity of sulphuric acid (two to three and a ha per cent.), which he allows to act at a temperature of 150° C. for tv to three minutes only, and then boils with water. In this way the larg portion of the fat acids are white enough to be used for candle-makin without previous distillation, while some twenty per cent. only of the needs to be distilled. The form of apparatus for the distillation of t free fatty acids produced in the sulphuric acid saponification is show in Fig. 20. T is the superheater, from which steam at 300° C. is pass into the retort D, which is previously filled to three-fourths of i capacity with melted tallow through the supply-pipes V V. The fat acids distil out of the tube U, are condensed by the worm S, and co lected by the receiver K.

(4) The superheated-steam process of Wilson and Gwynne, before alluded to. This is at present carried out in both England and Ge many. The apparatus devised by Mr. G. F. Wilson, of the Price Canc Company, of London, is shown in Fig. 21. The fat, previously heat in the flat vessel, A, by the waste-heat from the superheater below. flor into the retort C. This retort must be kept at from 290° to 315° C., as to this end is covered entirely above; the superheated steam at 315° comes into the retort by the tube to the side, and some twenty-four thirty-six hours is necessary to decompose and distil off a charge of fa If the temperature falls below 310° C., the decomposition is extreme slow, while much above 315° C., acrolein forms from the decomposition of the glycerine. The decomposition of fats by enzymes has also be made a working method quite recently. The enzyme contained in t castor-oil bean has been found best adapted for this. An emulsion fat, water, ten per cent. of ground castor-oil bean, and a small amou of free acid are used, when the decomposition proceeds rapidly.

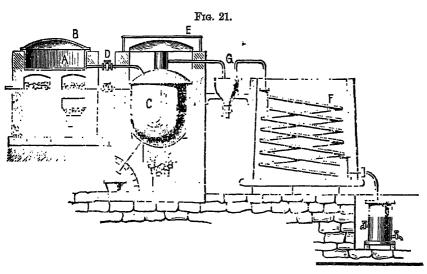
Before proceeding with the special processes of soap-making, stearing

candle manufacture, oleomargarine and glycerine production, it will be well to present in schematic way the complete treatment of a fat such as tallow. The accompanying scheme is taken from Post's "Chemische



Technologie," and shows the processes applicable and the products resulting from the technical utilization of tallow.

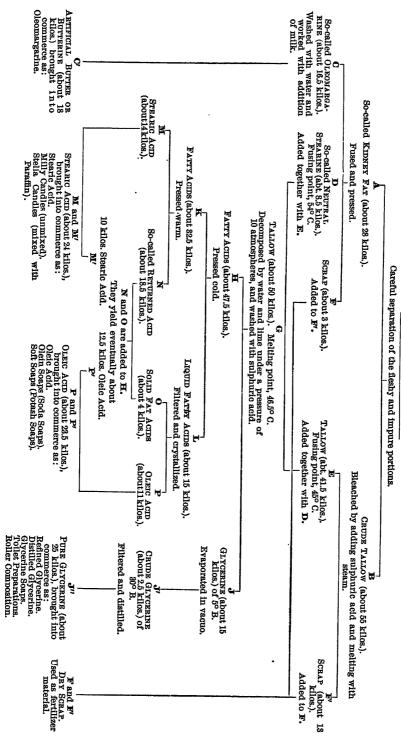
2. Practical Soap-making.—In the application of the first method of saponification of fats, that of the use of alkalies, we have, of course,



always a potash or a soda salt of the fatty acid formed, which, singly or admixed, constitute the products known as soaps. A very great variety of soaps are known, the appearance and properties of which vary according to the method of manufacture. We may classify the several methods of manufacture as follows:

### FRACTICAL UTILIZATION OF A FAT.

## 83 kilos. Crude Tallow (approximate yield of one Ox), Sulphuric Acid and Milk of Lime.



- (1) Boiling the fats in open vessels (coppers) with indefinite quantities of alkaline lyes until products of definite character are gotten. These are (a), soft soaps, in which the glycerine is retained, potash being the base; (b), the so-called "hydrated soaps," with soda for a base, in which the glycerine is retained, and of which "marine" soap may be taken as the type; (c), hard soaps, with soda for a base, in which the glycerine is eliminated, comprising three kinds,—curd, mottled, and yellow soaps.
- (2) Acting upon the fats with the precise quantity of alkali necessary for saponification without the separation of any waste liquor, the glycerine being retained in the soap. This includes (a) soaps made by the "cold process," and (b) soap made under pressure.
- (3) Direct union of the fatty acids, as in "red oil" and caustic alkali, or alkaline carbonate.

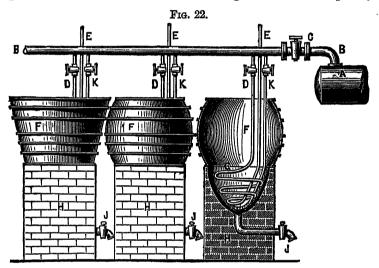
The general outlines of these methods may be indicated:

In the manufacture of soft soaps the drying oils are preferably used. In England whale, seal, and linseed oil are chiefly used, in Continental Europe hemp-seed, linseed, rape-seed, poppy, and train oils, and in the United States cotton-seed oil and oleic acid. A potash lye containing some carbonate is used, and frequently a portion of the potash is replaced by soda. The soft soaps, after being boiled to the necessary degree, are not salted, so that the glycerine and any excess of alkali remains in the soap. For use in wool-scouring this excess of alkali is, however, unsuited, so that neutral soft soaps are specially sought to be obtained. The method of making "hydrated" or "filled" soaps is very similar to that of soft soaps. Fatty matter and soda are run into the copper, and the whole is boiled together, care being taken to avoid an excess of alkali at first; when saponification has taken place, lye is cautiously added until the soap tastes very faintly of alkali, when the soap is ready to be transferred to the frames, without any salting or separating of the mixture. Marine soap, for use with sea-water, is made in this way, and is entirely cocoa-nut oil soap. The well-known Eschweger soap is also made by this general method from a mixture of cocoa-nut oil and other fats, saponified either separately or together, and containing the glycerine and water in the soap mass.

The manufacture of true hard soaps, which still constitute the great bulk of those made in England and the United States, requires more time and care than the varieties just mentioned. Melted fat and a quantity of soda lye of about 11° B., equal to one-fourth that needed for complete saponification, are simultaneously run into the copper and steam turned on. The "soap-copper," as shown in Fig. 22, is an iron kettle, or series of kettles, set in masonry, and equipped with pipes for both open and closed steam, and provided with an outlet for the discharge of the waste lyes when required. They may be used in series, or extra large single ones used. Strong lye should not be used at this first stage, or saponification will not take place. When the mixture becomes homogeneous, lye of 20° to 25° B., in amount equal to that taken before, may be cautiously added. It is now boiled until a sample taken

out has a firm consistence between the fingers. Common salt or a briu of 24° B. is now run in. A small sample removed on a spatula or trow should now allow clear liquor to run from it. The boiling is the stopped, and the copper should be allowed to stand at least two or thr hours. The contents now divide themselves into two portions, the upper consisting of soap-paste, containing water, and the lower consisting of "spent lye," holding in solution common salt and all the impurities of the liquors, together with glycerine. It should contain to caustic soda and no soap. After removing the spent lye from below the rest of the caustic soda lye is run in and the soap boiled up again At this stage the rosin is usually added for rosin or yellow soaps. The boiling is now continued until the frothing mixture boils quietly at

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becomes clear, the process being known as "clear boiling." The coppis then boiled with open steam and a small quantity of lye of 12° ] allowed to run in until the soap separates in flakes and feels hard whe cold, technically called "making the soap." Boiling is still continue for several hours to insure complete saponification, and it is then allowed to separate and harden. This procedure yields a curd soap if no ros. has been added. If, after a soap is "made," the lye in which it is su pended is concentrated to a point short of that necessary to produce hard curd soap, and it is then transferred to the cooling frames with certain quantity of lye entangled in it, these insoluble particles wil during the solidification of the soap, collect together and produce th appearance known as "mottling;" and the effect is heightened by the partial crystallization of the soap. The lye remaining in the caviti between the curds makes mottled soaps, the most suitable and real economical for washing clothes, etc., in hard waters, although not fe toilet purposes. Mottling is sometimes added, as the peculiar greenis mottle, which becomes red on exposure, characteristic of Marseilles ar Castile soaps, is produced by adding some solution of ferrous sulphato the copper when the soap is nearly finished (about four ounces of the salt to one hundred pounds of the fat); the precipitated iron protoxide suspended in the soap is greenish, but it becomes peroxide in contact with air, to which the change to a red color on exposure is due. Yellow soaps are made from tallow and rosin, the proportion of rosin varying from one-sixth of the total to an equal weight, or even more, according to the quality of the soap desired. In the presence of the sodium oleate from the tallow, the rosin acids saponify readily and coalesce to form a very uniform soap.

In smooth or "cut" soaps water or thin lye is added to the contents of the copper before the soap separates finally to form the curd, and is taken up in considerable amount, giving a smooth yet firm surface to the soap, instead of the hard, granular surface of the curd soap.

The so-called "cold process" requires the use of exact weights of well-refined fats and of caustic soda of a given specific gravity, the quantities being such that only just enough soda is present to completely saponify the fat. The materials are allowed to stand together for a short time and then thoroughly mixed in a copper provided with steam, agitating paddles, and kept at a temperature of not over 120° F. The reaction proceeds rapidly, and after some fifteen minutes the materials have so far united that they will not separate on standing, although the complete saponification of the materials may require days. They are then run out into the cooling-frames. It is obvious that soaps made in this way retain all the glycerine originally combined with the fatty acids disseminated through the particles of soap, and belong to the class known as "filled" or "padded" soaps, mentioned before. (See p. 68.)

When cocoa-nut oil alone is used, the temperature of working in this cold process need not be higher than 75° F. for summer and 90° F. in winter; if one-half tallow, 104° to 108° F.; and if two-thirds tallow, 113° to 120° F. is necessary.

Mixtures of cocoa-nut oil and other fats are frequently saponified in this way, the free acid of the cocoa-nut oil readily starting the process of saponification. A well-refined tallow can, however, be saponified in this way too, and mixtures of tallow and rosin worked up also into vellow filled soaps.

This combination of cocoa-nut oil with tallow and rosin can also take up on its saponification large quantities of water-glass and similar "filling" material, so that a very large yield of smooth filled soap is obtained. Thus a mixture of one hundred kilos. of cocoa-nut oil, seventy-five to eighty kilos. of rosin, three hundred kilos. of water-glass, one hundred to one hundred and fifty kilos. of tallow, and two hundred and forty kilos. soda lye of 33° B., will make eight hundred kilos. of a finished soap.

Saponification under pressure has also been frequently tried, the object being to shorten the time required for open boiling. In this case the quantity of alkali used must be accurately adjusted to the fat to be saponified, the glycerine is retained in the ultimate product. The process is carried out in an autoclave or pressure-boiler, the tempera-

ture is allowed to rise to about 310° F. (154.4° C.), equivalent to steam-pressure of sixty-three pounds to the square inch, and kept a this for an hour, when the contents are discharged into a cooling-fram

There remains to be noted the process of soap-making in which w start not with a fat, but with the free fatty acids, as in the "red oil or crude oleic acid obtained in stearine candle manufacture. 74.) These oleic soaps, as they are called, are made preferably from the oleine acid resulting from the saponification of tallow or palm oil k the lime process. That obtained in the distillation process is not so we adapted for use here. The oleic acid may be saponified either with ca bonate or with caustic alkali. The former process has the disadvantas that the escaping carbonic-acid gas causes a strong frothing which easily leads to boiling over. One hundred kilos, of the oleic acid obtains in the lime-saponification yield one hundred and fifty to one hundre and sixty kilos, of soap. The acid obtained by distillation always yield somewhat less. Frequently the oleic acid before saponifying is change by nitrous acid into the isomeric elaidic acid, which is as hard as tallo and from which a very fine soap can then be made resembling tallo soap, and capable of being worked at will into a curd soap or a co soap. If it be made with carbonate of soda, the copper is filled to on third its capacity with the oleic acid and the calculated amount of hal crystallized and half-calcined soda added, little by little, while tl heating and thorough agitation of the liquid is kept up. When the sor becomes thick and all foaming has ceased, the soap is filled at once in the forms to cool. The portion of crystallized soda used supplies a the water needed for the saponification.

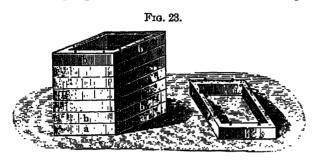
In saponification with caustic alkali, a strong lye (25° B.) is take No emulsion forms, but a lumpy, mortar-like mass, which, however, the alkali is more fully taken up and the lye becomes weaker, gradual goes over into ordinary soap-paste. The soap is separated by the addition of a strong lye instead of salting it.

After the finishing of the soap in the copper, it may either be pudirect into the cooling frame, or it may be transferred to mixing tank known as "crutchers," where various solutions or substances are incoporated with it prior to its being allowed to solidify.

Soap-frames are of two kinds, according as it is desired to cool the soap slowly or quickly. When slow cooling is required, as is always the case with mottled soap, wooden frames, usually of pine, are ended ployed. These are built up in horizontal sections, nine to twelve inched deep, each section lined with thin sheet-iron, as shown in Fig. 23. Mo curd and all yellow soaps are cooled rapidly in cast-iron frames of an desired shape and size. Such an iron soap-frame is illustrated in Fig. 24. The sides and ends of the frame are easily removed after the through solidification of the soap, and the block is then left upon the truck which served as the bottom of the frame. It is now ready for the cutting into slabs and bars. This is now almost universally done by me chinery, and the truck containing the hardened block is run at on into the large frame containing the cutting wires. Such a frame, a

though of smaller size, and used for slabs of soaps only, is shown in Fig. 25. The best piano-forte wire is necessary for these cutting frames, as the tension is very great when the soap is pressed through the wires.

While the soaps thus far spoken of are adapted for general or laundry purposes there is a distinct class of soaps known as toilet soaps.

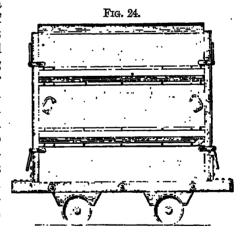


As these are to be applied to the skin they must answer other requirements, the most important of which is that they shall not contain any free alkali. Some dermatologists even demand that there shall always

be some unsaponified fat. We may distinguish transparent soaps, remelted soaps, and milled soaps.

Transparent soaps may be made either by the spirit process, in which case the stock soap is dissolved in alcohol, the solvent almost all distilled off, and the mixture then run into frames to gelatinize and solidify by gradual evaporation of the remaining alcohol, or the cold glycerine process. In this case the warm fatty materials employed (of

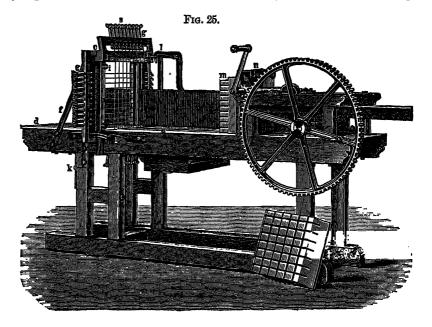
which castor oil is generally a large ingredient on account of the readiness with which it saponifies) are intimately mixed with soda ley; soluble coloring matters and essential oils or other scenting material are then stirred in and the whole allowed to stand. The glycerine which forms on saponification tends to cause the soap to take a transappearance. Perfect transparency can be obtained by the addition of more glycerine, or what accomplishes the same result, and is cheaper.



cane-sugar. This latter ingredient, however, makes the soap irritating to sensitive skins.

In the remelting of soaps, followed chiefly in England, several stock soaps may be mixed together, coloring and scenting materials added, and the mass heated in a steam-jacketed pan. If the mixture is rapidly agitated, enough air-bubbles may be worked in to enable the cake of soap to float in water, even after compression in the stamping press, producing a toilet soap which "floats" on water. The addition of some

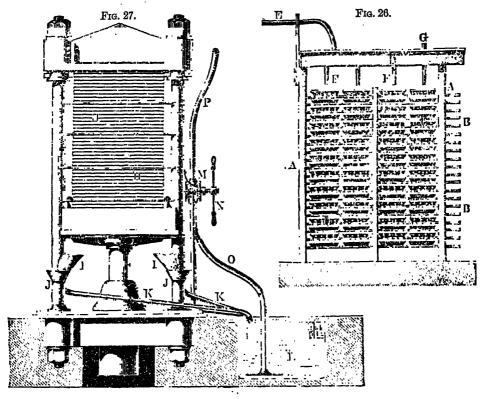
pearlash (potassium carbonate) is also made at times to improve the lathering power of the soap, but such soaps are alkaline and injurious to delicate skins. The finest toilet soaps, however, are made by "miling," a process first carried out in France. The bars of stock soap a first "stripped," or cut into slices by a slicing machine. The chips a dried in a warm air-chamber until only a few per cent. of water remain and then ground between heavy horizontal rollers of the milling muchine. At this stage the various coloring and perfuming ingredien are added, or unguents like lanolin and vaseline. The thoroughly miximaterial is then put into a cylindrical barrel, in which it is compressed by a piston and comes out as a continuous bar, which is cut into lengt



and stamped into cakes. The advantages of this method are, first, the inasmuch as no artificial heat is applied, delicate flower perfumes, et can be readily incorporated with the soap mass which it would be impossible to use with a remelted soap, because the heat would dissipate destroy the odoriferous matter; and, secondly, that as the resulting tablets usually contain only a small quantity of water, a given weight soap-cake or tablet generally contains a much larger quantity of actuse soap than another cake of the same weight prepared by remelting or I the cold process, whilst being harder and stiffer, it lasts longer, wasting less rapidly during use. Spherical cakes and wash-balls are finished I turning and polishing in a kind of lathe. Sometimes the polishing finished by the use of a cloth dipped in alcohol.

Shaving creams are made by the cold process from refined lard ar caustic potash, adding cocoa-nut oil in small amount to facilitate the making of lather.

3. Stearic Acid and Candle Manufacture.—For the extraction of stearic acid, the washed fatty acids (p. 65) are heated to the melting point and run into dishes or troughs made of tin, as shown in Fig. 26. These are placed in a room, the temperature of which is kept at 68° to 86° F. (20° to 30° C.), and left for two to three days, or until the contents have granulated, as the palmitic and stearic acids crystallize, when the dishes are emptied into canvas or woollen bags, which are carefully deposited between the plates of an upright hydraulic press, as shown in Fig. 27. Pressure is now exerted, increasing in degree until the flow



of the liquid oleic acid ceases. The hard, thin cakes of crude stearic acid so obtained are then melted down again with steam, and after settling, the melted acid run into the tin dishes and placed aside to cool. The temperature of the cooling-room in this case should be higher than before, or about 86° F. (30° C.). The blocks of stearic acid gotten are ground to meal, filled in bags of hair or wool, and then submitted to a second pressure, in a horizontal hydraulic press, the plates of which can be heated. In this press, a pressure of six tons per square inch, at temperatures of from 104° to 120° F. (40° to 49° C.), is reached. The cakes so obtained are melted by steam, a little wax being sometimes added to destroy the crystalline structure of the stearic acid, which somewhat unfits it for candle-making.

The yield of stearic acid obtained varies according to the fat use and the process of saponification employed. F. A. Sarg's Sons (Viennause three per cent. of lime under a pressure of ten atmospheres, and g ninety-five per cent. of crude fat acids and thirty per cent. of glycerin water (5° to 6° B.), and a final yield of forty-five per cent. stearic aci fifty per cent. of oleic acid, and five to six per cent. of glycerine. England, with the sulphuric acid and distillation process, they get six to seventy or even seventy-five per cent. of fat acids suitable for candl making, although inferior to that obtained in the lime process.

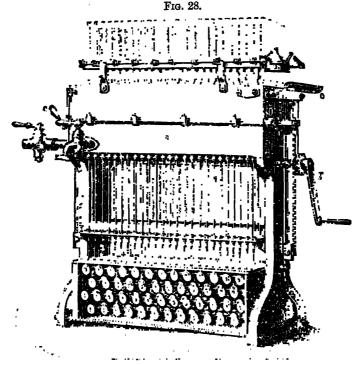
Palm oil is now used in enormous quantities for the production palmitic acid at Price's Candle Company's works, as well as by almo every candle manufacturer in Great Britain, about twenty-five thousar tons being annually consumed. In many continental countries a prohi itive duty prevents its employment. From this palmitic acid the fine composite candles are made by hot-pressing the distilled palmitic aci

Palmitic acid for candle-making is also made commercially, according to a process of St. Cyr-Radisson, by fusing oleic acid with a great excet of caustic potash, the products of the reaction being potassium palmetate, potassium acetate, and hydrogen. As carried out in Marseilles, the oleic acid and potash lye of 41° B. are put into an autoclave provide with a mechanical agitator, and heated until steam ceases to be give off, when the open manhole is closed, and the heat continued until 554 F. (290° C.) is reached. Decomposition now commences, and much hydrogen is given off through an escape-tube set in the lid of the boile At 608° F. (320° C.) the odor of the evolved gas suddenly changes, ar destructive distillation begins. This is arrested by blowing in steam once, and the contents are run out. The potassium palmitate is the washed, decomposed with sulphuric acid, the free acid washed ar distilled. The product of the distillation is white, and burns excellent when made into candles.

In the manufacture of candles, the first operation is the preparation of the wick. For dip-candles the wick is twisted, for others it is plaite and the kind of plaiting must also vary according to the material use Stearine candles require a moderately tightly-braided wick, paraff candles an extra tight braid, and for spermaceti and wax, on the othhand, the braids are measurably loose. After being twisted, or plaite the wicks are dried and then dipped into a pickling liquor, which is retard combustion and help in the destruction of the ash. The pick usually consists of a solution of boracic acid, ammonium phosphate, or ammonium chloride. Three plans of candle-making are at present i use,—dipping, moulding, and pouring. The first is employed for cor mon tallow candles, which are accordingly called "dips." frame holding the suspended wicks are placed troughs containin melted tallow, into which the wicks are repeatedly dipped. After eac dipping the adherent fat is allowed to cool sufficiently to retain a free coating on immersion. When the candles have thus grown to the property thickness they are left to cool and harden. These cheap "dips" ar however, now being replaced by small, moulded "composite" candle

as well as candles made from the softer, paraffin scale. Pouring is used only with wax candles, which cannot be moulded because of the adhering or cracking of the wax in removing it from the moulds. A well-made wax candle should show rings like a tree, where the different layers have been superposed. By far the greater number of candles are moulded, by which process they acquire a much more finished appearance. A form of frame in common use is represented in Fig. 28.

The materials in general use for candle-making are tallow, palmitic and stearic acids, paraffin, ozokerite or ceresine, spermaceti, and beeswax.



Very generally, several of these materials are admixed. Stearic candles have a small quantity of paraffin added to obviate the crystalline structure of the stearic acid; paraffin candles always have five to ten per cent. of stearic acid in them, to prevent the softening and bending of the paraffin when warmed. Spermaceti and beeswax are more expensive than the other materials, and are only used now for special purposes, as for church-candles and carriage-lights. Ozokerite gives the paraffin candle of highest fusing point, being some six degrees higher than any other variety of paraffin. Colored paraffin candles are made by dissolving the coloring matter (vegetable or aniline dyes, not mineral colors) in stearic acid, and then mixing this with the paraffin, which itself does not take up the color. Paraffin and other transparent candles must be filled in the mould very hot, and after all air-bubbles have escaped, the moulds must be rapidly cooled by a large flush of cold water

to prevent the paraffin, etc., from crystallizing and thus causing opacity Of interest in this connection is the table of illuminating equivalents or quantities of different illuminating materials necessary to product the same amount of light, prepared by Frankland.

Young's paraffin oil 1.00 gallon.	Sperm candles22.90 pound
American petroleum, No. 1. 1.26 gallons.	Wax candles26.40 pound
American petroleum, No. 2. 1.30 gallons.	Composite (stearine)29.50 pound
Paraffin candles18.60 pounds.	Tallow

- 4. OLEOMARGARINE, OR ARTIFICIAL BUTTER MANUFACTURE.—The mai ufacture of a butter-substitute from the solution of palmitin in olei which is known as oleomargarine, is a fat industry, but, because of i close relations to natural butter made from cows' milk, it will be considered as supplementary to the description of butter under milk industries. (See p. 284.)
- 5. GLYCERINE MANUFACTURE.—For many years after the develop ment of the soap and candle industries, no attempt was made to recove the glycerine which was liberated in the saponification. Its application tions in medicine and for technical purposes have made it importar to extract and purify it, however, and it has now assumed almost equiimportance with the other fat constituents. The two methods of sapon fication, by which glycerine has been obtained on a large scale, are the process of Wilson & Payne, of decomposing the fats by superheate steam and after distillation (see p. 65), and the lime autoclave proces (See p. 64.) In the distillation process, however, by suitab arrangement for fractional condensation, it is found possible to co centrate the aqueous glycerine in the process of distillation. Care mu be taken that the temperature of 600° F. (315° C.) is not exceeded, ar that plenty of steam is present, otherwise some glycerine is decor posed and acrolein is formed. In the Milly process, after the decor position of the fat is completed in the autoclave, the contents are blow out into a tank and the "sweet water" (glycerine) is run off. concentrating may be done in contact with air or preferably it may l worked in some form of vacuum evaporator. Evaporation is continue to 26° B. (1.220 specific gravity), when the glycerine is of a browning color, and is known as "raw," in which state it is sold for many pu poses, and contains about ninety per cent. of glycerine and traces on of mineral impurities. At Price's Candle Company's works the furth purification is conducted as follows. The raw glycerine, specific gravi-1.240 to 1.245, is heated in a jacketed pan with that kind of anim charcoal known as ivory-black, and is then distilled; this alternate tree ment is repeated as often as is necessary. The distillation is performe with superheated steam in a copper still provided with copper fraction condensers, the still being also heated externally; the operation is pe formed at as low a temperature as is consistent with distillation, usual about 440° F. (227° C.).

It is obvious that in soap-making, as enormous quantities of the fa are decomposed, corresponding quantities of glycerine go into the spe lyes. It is only very recently that it has been attempted to recover this glycerine. The two processes at present in use are those of Jobbins and Van Ruymbeke and of Garrigues. Another suggestion of more recent date is to deglycerinize all fats before saponifying them. The process of Michaud Frères, of Paris, as carried out by the Continental Glycerine Company, of New York, realizes this idea very successfully.

According to their patent "the fatty matter is subjected in a close vessel to the action of the steam, at a pressure of one hundred to one hundred and thirty pounds per square inch, and at corresponding temperature in presence of one-fourth to one-third part of its weight of water and one-fifth to three-fifths per cent. of its weight of the oxide of zinc, known commercially as zinc white, or a like proportion of zinc powder or zinc gray, which is a residue in the treatment of zinc, being a mixture of zinc with its oxide. . . The very small proportion of mineral substance used is sufficient for dispensing with the acid treatment applied for decomposing lime soap, and the product obtained, consisting almost exclusively of acid fat, can be converted by the acids usually employed into soap or candles. In soap-making, the dissolving powers of the caustic alkalies remove all objections to the presence of the zinc if it should be used in excess. The reducing power of the zinc powder prevents discoloration of the acid fats such as results from the ordinary treatment." The glycerine thus produced finds a ready sale, as it runs from the evaporators, and from it, as "crude," ninety-six per cent. of pure glycerine can be obtained.

5a. NITRO-GLYCERINE AND DYNAMITE.—In 1847 Sobrero discovered a very interesting derivative of glycerine, and in 1862 A. Nobel gave it to the world as a technical product of the greatest importance. When strong glycerine is gradually added to a well-cooled mixture of very strong nitric and sulphuric acids, it is converted into glyceryl nitrate, or nitro-glycerine. For the manufacture of nitro-glycerine on a large scale, Nobel recommends that one part of good glycerine be allowed to flow in a thin stream into a well-cooled mixture of four parts of concentrated sulphuric acid and one part of the very strongest nitric acid (1.52) specific gravity), the mixture being contained in a wooden vessel lined with lead. Means should be provided by which the mixture can at once be run into a large quantity of water should the action threaten to become too violent. On standing, the nitro-glycerine separates as a layer on the surface of the acid, and is skimmed off and washed with water and solution of sodium carbonate to get rid of every trace of free acid. Or, according to the same authority, a mixture is made of one part nitre with 3.5 parts of sulphuric acid (1.83 specific gravity), the mixture cooled to 32° F. (0° C.), and the liquid poured off from the acid potassium sulphate, which separates out; into this liquid the glycerine is slowly dropped, the mixture poured into water, and the separated nitro-glycerine washed thoroughly and dried. The yield is two hundred and twenty-three per cent. of the glycerine used.

It has been suggested to mix the glycerine beforehand with the sulphuric acid, and then run this mixture into the nitric acid, and it is į

claimed that the elevation of temperature is less than when the ord nary method is followed; but the process does not seem to have be satisfactory in practice when tried in England.

When absorbed by infusorial earth, "kieselguhr," sawdust, microwder, or other inert porous material, nitro-glycerine forms the different varieties of dynamite, and, when combined with gun-cotton, constitutes the explosive known as "blasting gelatine."

### III. Products.

1. Purified Oils, Fats, and Waxes, and Products from the sam—Most of the important oils, fats, and waxes have already been describe as raw materials, and the methods of purifying them have been note. The purified oils are in some cases the final products sought, and, some cases, only improved raw materials for the main industries, lil soap-making, candle-making, and glycerine extraction. These purified oils having, therefore, been referred to as raw materials, will not be further noted. A number of side-products, obtained with or produce from these oils, remain to be mentioned.

One of these minor products of great value is the oil-cake, or corpacted mass of crushed seeds or nuts, from which the oil has been expressed or extracted. This contains all of the woody fibre and miner matter of the seed or nut, the residue of oil or fatty matter not extracted, and, what gives it special value, the proteids or nitrogenous constituents. The oil-cake thus becomes a most valuable cattle food ar a basis for artificial fertilizers. The following table gives the comp sition of a number of the most important oil-cakes:

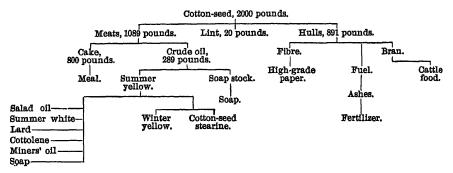
	Water.	Fat.	Non-uitrogen- ous materials. Woody fibre.	Ash.	Protein material.	Nitrogen per cent
Earth-nut cake Cotton-seed cake Rape-oil cake Colza-oil cake Sesame-oil cake Beech-nut cake . Linseed cake Camelina cake Poppy-oil cake . Sunflower-oil cake . Hempseed cake Palm-nut cake Cocoa-nut cake	11.50 18.00 10.12 11.35 10.35 11.40 10.56 9.60 9.50 10.20 10.00 9.50 10.00	8.80 7.50 9.23 9.00 10.10 8.50 9.83 9.20 8 90 8.50 8.26 8.48 9.20	31.10 51.00 41.93 42.82 38.80 49.80 44.61 50.90 37.67 48.90 48.00 40.95 40.50	7.25 8 50 6.48 6.28 9.80 5.30 6.50 7.00 11.43 11.40 12.24 10.62 10.50	41.85 20 00 31.88 80.55 31.93 24.00 28.50 23.80 82.50 21.00 21.50 80.40 80.00	6.80 2.90 5.00 4.50 5.00 8.20 4.25 8.60 5.00 2.40 8.30 4.50

It will be seen in this table that they vary in proteids or flesh-formir constituents quite widely. All of these cakes, however, are too rich i these proteids and in fats to be used unmixed as fodder. They are, practice, mixed with cereals, hay, and straw, and then constitute a valuable food. The ash is, moreover, very rich in phosphoric acid and potash, and this explains its value for fertilizer manufacture.

Thus it is stated that, as a fertilizer, one ton of cotton-seed-hull ashes has as much value as four and one-half of average hard-wood ashes, or fifteen of leached hard-wood ashes.

The amount of oil-cake obtained from the expression of the different vegetable oils is enormous. Thus it is stated that one short ton of cotton-seed (constituting forty per cent. of the raw cotton) will yield eight hundred pounds of cotton-seed cake and forty-five gallons of crude cotton-seed oil. The amount of crude cotton-seed annually obtained in the United States is estimated at four thousand million pounds, half of which only is required for sowing.

The accompanying table, prepared by Grimshaw, will show how thoroughly the cotton-seed is now utilized:



An important manufactured oil is what is known as "Turkey-red oil," used in the process of alizarin dyeing. (See p. 539.) There are, in fact, two entirely distinct oils known under this name. One is simply an inferior grade of olive oil, that known as "Gallipoli oil," and for this particular use is prepared from somewhat unripe olives, which are steeped for some time in boiling water before being pressed. This treatment causes the oil to contain a large proportion of extractive matter, and hence it soon becomes rancid. This preparation has long been used in the old process of Turkey-red dyeing, under the name huile tournante. The other, used for producing alizarin reds by the quick process, is the ammonium salt of sulpho-ricinoleic acid (C<sub>18</sub>H<sub>33</sub> (HSO<sub>3</sub>)O<sub>3</sub>), a body which is obtained mixed with unaltered glycerides and with products of its decomposition by the action of sulphuric acid upon castor oil.

From linseed oil, as the most important of the class of drying oils, is prepared a product of great value for paint and varnish manufacture. (See p. 112.) What is called "boiled oil" is linseed oil, which has been heated to a high temperature (130° C. and upward), while a current of air is passed through or over the oil, and the temperature increased until the oil begins to effervesce from evolution of products of decomposition. By adding litharge, red-lead, ferric oxide, or manganese dioxide, or hydrate, during the process of boiling, the oxidation and consequent drying of the product are still further facilitated. The nature, proportion, and mode of adding these substances are usually kept

PRODUCTS.

jealously secret. Lead acetate and manganous borate are among the most approved. The action of some, at least, of these "dryers" (e. g compounds of manganese) seems to be that of carriers of oxygen, while litharge dissolves in the oil and acts partly as a carrier of oxygen and partly as the base of certain salts which oxidize very rapidly.

Many of the fatty oils and notably some of the non-drying oils ar capable of being thickened and increased, especially in specific gravit and viscosity, by having a stream of air blown through them. The products of this treatment are known as blown oils or oxidized oils. The are not resinified as when the drying oils are boiled with driers, by become thick and viscid like castor oil. This property is taken advartage of, therefore, in the production of heavy viscid products, whice are used in admixture with mineral oils for the purpose of preparing lubricants for heavy machinery. While cotton-seed, rape, olive, earth nut, lard, and linseed oils have all been utilized in this way, the twenty the second of the purpose of preparing the commonly employed are rape and cotton-seed oils.

In carrying out the blowing operation, the oil is usually heated to 70° C. (138° F.) or slightly more, and air is then blown in through a vertical pipe which passes down nearly to the bottom of the kettle the air being itself heated to the same temperature. In a short time the oil begins to oxidize and the temperature to rise. The steam is the shut off from the heating coils, and care must now be taken that the temperature does not rise above 80° C. (176° F.). The process usuall lasts from twelve to forty-eight hours, according to the nature of the obeing treated and the character of the product desired. By continuing the operation, products may be obtained of specific gravity as high a from .985 to .999 even.

Blown oils vary in color from a clear yellow to a dark reddish yellow and have a peculiar and somewhat disagreeable odor. They are verification, as dense or denser than castor oil, from which they differ in no being readily soluble in alcohol but in being soluble in petroleum spirisheir perfect miscibility with heavy mineral oils is, however, the chief advantage. The percentage of free fatty acids is usually increased by the blowing operation and the percentage of insoluble fatty acid decreased, owing to the formation of soluble oxyacids.

The following table from Lewkowitsch ("Oils, Fats, and Waxes, 2d ed., p. 734) will show the change undergone by rape oil in cons quence of the blowing operation:

	Specific gravity at 15.5° C.	Free acid as oleic.	Saponifi- cation value.	Iodine value.	Insoluble acids.	Soluble acids.
Rape oil	0.9141 0.9275	5.10 5.01	173.9 183	100.5 88.4	94.76	0.52
Same, 20 hours' blowing	0.9615	7.09	194.9	63.2	85.94	10.02

2. Soaps.—In noting the processes for practical soap-making, the following classes of soaps were indicated: (1) compact soaps, including (a) curd soaps; (b) mottled soaps, and (c) yellow soaps; (2) smooth

or cut soaps; (3) filled or padded soaps; and (4) soft or potash soaps. The most important difference between the compact, cut, and filled soaps is the amount of water present in the soap. In the compact soap it may vary from ten to twenty-five per cent., in the cut soap from twenty-five to forty-five per cent., and in the filled soap from forty-five to seventy-five per cent. In addition, the filled soap contains the glycerine, spent lye, and other impurities of the soap copper.

The following table of analysis, by Mr. C. Hope, as quoted by Allen,\* will illustrate the composition of a variety of soaps belonging to these several classes:

NAME OF SOAP.	Materials,	8 3	Soda existing as soap.	Silica,	Soda as silicate.	Sodium carbonate and hydrate.	Neutral salts, lime, and iron oxide.	Water.	Total,
White, No. 1 White, No. 2 White, No. 2 White, No. 3 White, No. 4 Cold water, No. 1 Cold water, No. 1 Marseilles, No. 1 Marseilles, No. 1 Mottled Glasgow almond Pale rosin, No. 1 Pale rosin, No. 1	seed oil Olive oil Chiefly olive oil Palm oil Palm-nut oil Tallow and rosin Tallow and rosin Tallow and rosin		6.82 6.90 6.23 7.98 7.00 7.58 7.27 6.76 4.14 7.22 5.00	1.07 2.34 .06 .06 .12  .02 5.64 .04 .42	1.59	.77 .89 1.62 .92 2.76 .10	.72 .39 .26 1.00 .82 1.01 1.03 1.22 .76 2.58 1.70 .51 .60 .90	32,20 36,54 38,14 17,44 38,18 19,70 28,20 32,35 38,70 31,30 42,88 81,22 45,00	99.84 99.82 99.82 100.21 99.86 95.19 99.75 99.98 100.00 99.80
Pale rosin, No. 8 Milling Yellow (for foreign markets) Marine (for emigrants)	Tallow and rosin Not mentioned	89.92 63.06 10.90 19.42	7.25 1.36	.62 .02 .03 9.00	.25 3.98	Trace	1.81 1.90 3.27 5.64	52.40 27.47 84.00 53.32	100.00 99.56

Two of these samples, those designated as "mottled" and "marine," were prepared by the "cold process" (see p. 70), which accounts for the totals being appreciably less than 100.00, as the glycerine was retained in the soap.

The chief soaps of pharmacy, as analyzed by M. Dechan, † are composed as follows:

Description of Soap.	Fatty acids.	Combined al- kali.	Free alkali.	Silica.	Sulphates and chlorides.	Insoluble matter.	Water.	Insoluble in alcohol.
Hard soap (sapo durus) White Castile soap (s. Cast. alb.) Mottled Castile soap Tallow soap (sapo animalis) . Soft soap (sapo mollis)	81.5 76.7 68.1 78.8 48.5	9.92 9.14 8.9 9.57 12.6	.08 .09 .19 .28 .38	.00 .00 .15 .00	.28 .36 .63 .47	0.20 0.90 0.80 0.40 1.00	10.65 13.25 21.70 12.50 89.50	0.50 0.60 1.30 1.10 1.60

<sup>\*</sup> Allen, Commercial Organic Analysis, 2d ed., vol. ii, p. 272.

<sup>†</sup> Pharmaceutical Journal [3], xv, p. 870.

Toilet soaps do not differ in essential composition from the best compact and cut soaps, as given above, but they are perfumed and give small additions of cosmetic or hygienic preparations. They are pr pared in one of three ways: (1), by a melting of plain soaps; (2), cold perfuming and pressing of finely-divided plain soaps; and (if direct preparation from the raw soap-making materials.

Transparent soaps are obtained by dissolving the soaps in alcoh and drying the solution in moulds,—a slow process. (See also p. 72.)

Glycerine soaps are obtained by dissolving the soaps in glycerine I the aid of heat. Thy glycerine imparts a strength to the lather.

- 3. Candles.—The candle-making materials have already been en merated. (See p. 74.) Tallow and wax candles were the earliest in us Stearine candles, known also under the name of Milly candles, from the French inventor of several of the processes of saponification, came in use in 1831. About the same time paraffin, first obtained in quanti from bituminous shales, and later from ozokerite and petroleum, w used for candle-making. These are also known under the name "Belmontin candles," from the locality of the J. C. & J. Field candl works, in London. Candles of mixed stearic acid and paraffin, und the name of Stella or Apollo candles, were then manufactured. TI Galician ozokerite is also purified by sulphuric acid, and under tl name of ceresine (see p. 35) is used in Austria for candle manufactur Beeswax and spermaceti, as before stated, are high-priced material and are used for special classes of candles. The paraffin and steari candles and those which are mixtures of these materials are now mo generally in use.
  - 4. OLEOMARGARINE OR BUTTERINE. (See p. 289.)
- 5. GLYCERINE AND NITRO-GLYCERINE.—The chemical which is liberated along with the fatty acids when the fats are saponific by any of the various processes already narrated is a triatomic alcoholic called glycerine. When purified and made absolute, it is a colorles viscid liquid, without odor, but with a pronounced sweet taste. The specific gravity of the absolute glycerine is about 1.266 at 15° C. Who kept for a long time at 0° C., rhombic crystals are formed, their pr duction being greatly facilitated by the presence of a ready-form The crystals are hard and gritty, but deliquescent. under ordinary pressure at 290° C., not without decomposition. highly hygroscopic, and is miscible with water in all proportions. cerine is miscible with alcohol in all proportions, but is insoluble in chl roform, benzene, petroleum spirit, carbon disulphide, or fixed oi Glycerine is nearly insoluble in ether, from which it separates ar alcohol or water. When glycerine is heated with a dehydrating age: (e. g., concentrated sulphuric acid), irritating fumes of acrolein (acryl aldehyde), C.H.OH, are evolved, smelling of burning fat. By far the largest application of glycerine is for the manufacture of nitro-glycerin but it is also employed extensively in the manufacture of toilet soar for filling gas-meters and tubes in situations liable to be exposed great cold, and in pharmacy and medicine. It is also used for the pre

ervation of food products, and for the treatment (scheelizing) of wine, vinegar, and beer.

Nitro-glycerine is a heavy, oily liquid of 1.600 specific gravity at The commercial preparation is usually yellowish to brownish. although the pure oil is colorless. It has no marked odor, but is sensibly volatile at ordinary temperatures, and the vapor causes a violent headache in those unaccustomed to it; but people constantly employed in mixing and handling dynamite do not suffer from the effects. Nitroglycerine has recently been employed in medicine, especially for the treatment of angina pectoris. Nitro-glycerine is not readily inflammable, and when ignited commonly burns with a greenish flame, without The most characteristic property of nitro-glycerine, and explosion. that which gives it by far its most important application, is that of exploding with extreme violence when smartly struck or compressed or when dropped on an iron plate heated to 257° C. The presence of free acid in nitro-glycerine, however, makes it liable to spontaneous decomposition and explosion.

Nitro-glycerine is easily saponified by alcoholic potash, and is reduced by various deoxidizing agents.

Nitro-glycerine in undiluted state is only exceptionally used now for explosive purposes, as in "torpedoing" oil-wells. For blasting purposes it is mechanically mixed or absorbed in some finely divided solid material.

Thus, Dynamite No. 1 contains seventy-five per cent. of nitro-gly-cerine mixed with twenty-five per cent. of infusorial earth or kieselguhr. This mixture is then packed in cartridges of paraffined paper, constituting the "stick" of dynamite.

Mica powder consists of fine mica scales in which about fifty per cent. of nitro-glycerine is absorbed.

Next in order come explosives in which with the nitro-glycerine is combined an active base, either a nitrate or a mixture of nitrate and combustible substance, like charcoal or sulphur. The best known are:

Dynamite No. 2 contains forty per cent. of nitro-glycerine, sodium nitrate thirty-eight, sulphur six, resin eight, and kieselguhr eight.

Dynamite No. 3 contains nitro-glycerine fifteen, and eighty-five of a mixture of sodium nitrate, coal, and sodium carbonate.

Vulcan powder contains nitro-glycerine thirty, sodium nitrate fiftytwo and five-tenths, and sulphur and charcoal seventeen and five-tenths.

Atlas powder A and B contains respectively seventy-five and fifty of nitro-glycerine, with sodium nitrate, wood fibre, and magnesium carbonate.

Hercules powder is similar to Atlas powder B, but contains only forty per cent. of nitro-glycerine and forty-five of sodium nitrate.

Vigorite contains, with thirty of nitro-glycerine, potassium chlorate forty-nine, potassium nitrate seven, wood pulp nine, magnesium carbonate and moisture five.

Forcite contains nitro-glycerine seventy-five, potassium nitrate eighteen, and gelatinized cotton seven. This latter ingredient is made

by treating finely pulped cotton with steam under pressure until converted into a jelly, which is then mixed with the nitro-glycerine and the finely powdered nitrate added. The resulting product is a plastic mannesembling rubber, impervious to water, and relatively safe to handle Still another and more recently developed class of explosives at those in which nitro-cellulose or gun-cotton is combined with nitroglycerine. The most important are:

Blasting gelatine or gelatine dynamite, which is a mixture of abore eighty parts of nitro-glycerine with twenty of nitro-cellulose. An unnitrated cotton or trinitro-cellulose interferes with the solution of the nitro-glycerine. The addition of four per cent. of camphor render the mixture incapable of exploding when struck by a rifle bullet, but can be detonated by a strong dynamite cap.

Cordite, which has been adopted by the English government as standard "smokeless powder," contains nitro-glycerine fifty-eight, gu: cotton thirty-seven, and vaseline five. The nitro-glycerine and gu: cotton are first mixed, 19.2 parts of acetone added, and the pasty ma kneaded for several hours. The vaseline is then added and the mixtu: again kneaded. The paste is then forced through fine openings to for threads, which are dried at about 40° C. until the acetone evaporate The threads are then cut into short lengths for use. They resemble brown twine.

There are analogous explosives known as "smokeless powders" is which no nitro-glycerine at all enters, but which are merely cellulounitrates or gun-cotton gelatinized and dried, as just described.

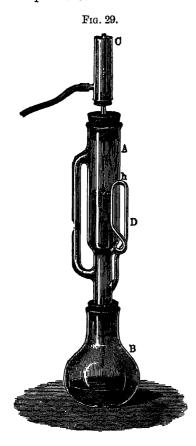
Picrates and picric acid are sometimes used; but, while powerful epolosives, they are considered too unstable. *Melinite* and *Lyddite* are of this class.

### IV. Analytical Tests and Methods.

1. For Oils and Fats.—The total amount of oil in any particula oil-seed or other material is always an important matter to determin This is best effected by treating the finely divided and previously drie substance with solvents under such conditions as to insure complete extraction. A form of apparatus in which this can be effected with the minimum amount of the solvent is what is called an oleometer. One of the best of these is the Soxhlet extractor, shown in Fig. 29, where is represents the extractor, B the distillation flask, C the condenser, an D the siphon-tube which empties the extractor. A is filled to three fourths its capacity with the powdered oil seed, and the bulb B is hal filled with the petroleum-ether, carbon disulphide, or proper solven. The apparatus is then connected, as shown in the cut. Filter thimble stamped out of Swedish filter paper are largely used in this connectio to contain the weighed substance. They slip in the extractor and can be weighed before and after the extraction.

To recover the oil from its solution in the ether or other liqui employed, the solvent should be distilled off at a steam heat, and th last traces of it removed by placing the flask on its side and heating in the water-oven until constant in weight.

The physical constants which are relied upon as characteristic in the case of oils and fats are specific gravity, and in the case of solid fat fusing points. Boiling-points are not relied upon, because of the particle decomposition which fixed oils usually undergo when heated to his temperatures.



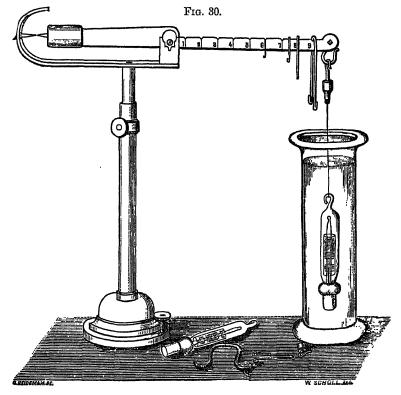
Specific gravity in the case of tl liquid oils may be determined with tl aid of the specific gravity bottle, tl Sprengel tube, or the Westphal hydr static balance. The first of these is well known from elementary works ( chemistry as to need no description her The Sprengel tube is a U-shaped tub of which the two ends terminate in car illary tubes bent at right angles to tl sides. The tube is completely filled wit oil by immersing the open end of the tube in the liquid and gently suckir the air out from the other orifice. U-tube is then placed in the mouth of conical flask, containing boiling wat (if the determination is to be made a 100° C.) or water at any other fixe lower temperature. The excess of c that escapes at the orifices of the tul is wiped off with soft paper, and who the expansion ceases the tube is remove wiped dry, allowed to cool, and weighe The calculation can then be made, know ing the weight of the tube empty ar filled with water at the same temper ture, or at 15° C. The Westphal be ance is shown in Fig. 30. The the mometer or other plummet used di places a definite volume of the oil.

that the loss in weight is the weight of this bulk of the oil under examnation.

The melting-point of solid fats may be gotten with considerable acc racy by the melting-point method in general use in chemical laboratoric A capillary tube is filled with the fat while it is in the melted stat and then, after allowing it to cool and solidify, attach the tube to to stem of a delicate thermometer and immerse the thermometer in a beak of water, which is then gradually heated until the melting-point of to fat is reached, and it liquefies in the capillary tube. The temperature which this takes place is at once read off on the attached thermomete

To insure accuracy it is desirable to immerse the beaker of water in an outer vessel also filled with water, to which the heat is applied.

The solidifying point of the liberated fatty acids in the case of the analysis of an individual fatty oil is frequently determined, and is known as "the titer test." One hundred grammes of the fat under examination are saponified (see p. 88), the separated fatty acids freed from water and filtered through a dry plaited filter and allowed to solidify. The fatty acid mixture is then carefully melted and a rather long test-tube filled to more than half its capacity. The tube having been fastened by means of a cork into a wide-mouthed bottle, a delicate thermometer indicating one-tenth of a degree is inserted into the fatty acids so that the bulb reaches the centre of the mass. When a few crystals appear at the bottom of the tube the mass is stirred by giving the



thermometer a rotary movement, first to the right and then to the left. The mass is thus stirred without allowing the thermometer to touch the sides of the tube until it becomes cloudy throughout. The temperature will fall steadily and then rise suddenly some tenths of a degree and become stationary for a brief period of time. The reading taken at this moment is called the "titer test" or solidifying point.

Of great importance with some of the fatty oils, such as sperm, rape, and lard oils, is the question of viscosity, and in quite a number the

question of cold test. The methods of determining these have been given in detail under mineral oils. (See p. 43.)

In some special cases the use of the oleo-refractometer, an instrument for noting the difference in refractive indices of oils, has proven valuable. Thus, true butter fat can be distinguished by this means from butterine or oleomargarine.

A number of chemical reactions have been taken at one time or another for the purpose of distinguishing between the different animal and vegetable oils and fats. Many are unreliable and the results contradictory, because dependent upon special conditions, so that no great value attaches to them. This statement may fairly be said to apply to most of the color-reactions which are gotten by the action of sulphuric and nitric acids upon the different oils and to the differences in elevation of temperature caused by the addition of concentrated sulphuric acid to the fatty oils.

Of much greater value, as affording general reactions for the distinguishing of the different oils and fats, are two processes of treatment now very generally adopted by chemists in the analysis of fats and fatty oils,—viz., the saponification value and the bromine or iodine absorption value.

The saponification value (known also as Köttstorfer value) indicates the number of milligrammes of potassium hydroxide required for the complete saponification of one gramme of the fat or wax. The determination is carried out as follows: About 1.5 to 2.5 grammes of the fat are treated with twenty-five cubic centimetres of one-half normal alcoholic potash; when saponification has taken place, one cubic centimetre of an alcoholic solution of phenol-phthalein is added and the liquid titrated with one-half normal hydrochloric acid. A blank experiment is then made by titrating twenty-five cubic centimetres of the alcoholic potash alone, and the difference in the volumes of the acid used gives the volume of the potash solution neutralized by the fat, which is then calculated to milligrammes of potash for one gramme of fat used. The following are a few examples:

OIL OR FAT.	Milligrammes of KOH per one gramme of fat. Saponifica- tion equivalent.	Average saturation- equivalent.
Tallow Lard. Cocoa-nut oil Palm-nut oil Olive oil Cotton-seed oil Rape oil Linseed oil Butter fat Butterine Sperm oil Spermaceti Beeswax	193.2 to 198.0 192.0 to 196.5 246.2 to 268.4 220.0 to 247.6 191.0 (average) 193.8 (average) 173.3 (average) 191.3 (average) 221.5 to 232.4 193.5 to 196.5 123.4 to 147.4 128.9 (average) 94.5 (average)	286.9 288.8 218.4 240.8 298.7 289.4 828.7 298.2 247.0 287.7 880 to 454 435.2 598.6

The numbers in the last column designated as "saturation equiv lents" represent the number of grammes of the oil or fat in questic that would be decomposed by one equivalent of potassium hydroxide grammes, and is obtained by dividing the percentages of potassium h droxide required into 5610, which is the molecular weight of KOH mutiplied by 100. The figures given as "saponification equivalents" a most generally used and are sufficiently characteristic to allow of the recognition of adulteration in many cases.

The bromine and iodine absorption methods depend upon the pecentage of bromine or iodine taken up by the oil under conditions i tended to insure the formation of addition-compounds only. The fat acids of the acetic or stearic series are saturated bodies, which do n form addition-compounds with bromine or iodine, while the acids of the acrylic or oleic series combine with two atoms of a halogen and the of the propiolic or linoleic series with four atoms of a halogen. The glycerides of the acids of these three series behave similarly to the fracids, so that the determination of the percentage of bromine or iodinassimilated gives a measure of the proportion of olein as against partial and stearin in a fat, and of the linolein of a drying oil as corpared with the olein of a non-drying oil.

Hübl's procedure for determining the iodine absorption is as follow He employs an alcoholic solution of mixed iodine and mercur chloride: twenty-five grammes of iodine are dissolved in one-half lit of ninety-five per cent. alcohol, free from fusel oil, and thirty gramm of mercuric chloride in another one-half litre of the same. The tv solutions are then mixed after filtration, if necessary, and used aft twelve hours' standing: it must also be standardized immediately befo or after use. About .2 to .4 gramme of oils or .8 to 1 gramme of sol fats is weighed off and dissolved in ten cubic centimetres of chloroforr. twenty cubic centimetres of iodine solution are added, and successiadditions of five or ten cubic centimetres are made until, after two hour the solution has a dark brown tint. It is best to leave it for from for to six hours protected from the light before the next step. From ten fifteen cubic centimetres of a ten per cent. aqueous solution of pote sium iodide are then added and one hundred and fifty cubic cent metres of water. The free iodine is then titrated with a solution sodium thiosulphate containing twenty-four grammes per litre. amount of iodine absorbed is calculated into units per cent. of the fa and may conveniently be termed the iodine degree. Since one cubic ce timetre of the thiosulphate solution is equivalent to .0127 of iodine, tl number of cubic centimetres of this sulphate used multiplied by 12 and divided by the weight of fat used will give the iodine figure of the fat or oil. This number appears to be tolerably constant for each o or class of oils, and is highest with the vegetable drying oils, as will seen by this short list taken from Hübl's table: linseed oil, 158; hem seed oil, 143; cotton-seed oil, 106; olive oil, 82.8; lard, 59; palm oil, 51. tallow, 40; cocoa-nut oil, 8.9. The values thus obtained are quite co stant, provided an excess of iodine of not less than thirty per cent. employed and the operations be carried out under exactly the same conditions.

Wijs proposes a solution which has better keeping qualities than the Hübl solution, and in consequence may be more uniformly depended upon for accurate results. He dissolves separately 9.4 grammes of iodine trichloride and 7.2 grammes of iodine on the water-bath in glacial acetic acid, taking care that the solutions are protected from absorbing moisture while solution is taking place. The two solutions are then poured into a 1000 cubic centimetre flask and the contents filled to the neck with glacial acetic acid. The chloroform used in the Hübl process is preferably replaced by carbon tetrachloride, which, however, must not contain any oxidizable substances. The test is carried out as with the Hübl solution, but the time for standing is much shorter.

The method which, however, seems simplest and shortest is that of Hanus. In this method the iodine solution is prepared by dissolving 13.2 grammes of pure iodine in one litre of pure glacial acetic acid (ninety-nine per cent.), and to the cold solution add three cubic centimetres of bromine or sufficient to practically double the halogen content when titrated against the thiosulphate solution, but with the iodine slightly in excess. The thiosulphate solution, starch paste and potassium iodide solution are as in the Hübl method. Proceed as in the Hübl method, substituting thirty cubic centimetres of the Hanus iodine reagent for that of Hübl, stirring the solution before adding the water, and instead of adding fifteen or twenty cubic centimetres of potassium iodine use only ten cubic centimetres. Only half an hour is required in this case for the full action of the iodine on the oil, instead of three hours or more.

Certain thermal tests, or those measuring the heat of reaction, are used in some cases. The Maumené test or the heat developed on addition of strong sulphuric acid has long been known, but is not much relied upon at present. The bromination test measures the rise in temperature caused when fats absorb bromine, both the fat and the bromine being used in solution in chloroform or carbon tetrachloride, and the vessel in which the reaction is carried out being insulated by non-conducting packing. The results bear a fixed relation to the iodine absorption number and one can be calculated approximately from the other.

For qualitative detection only, cotton-seed oil can also be identified in lard by Becchi's test, with an alcoholic solution of silver nitrate, which gives a maroon color in the presence of the cotton-seed oil, or still more certainly by Halphen's test, using a mixture of equal volumes of amyl alcohol and carbon disulphide containing about one per cent. of sulphur in solution and heating to boiling with this reagent.

The adulteration of the fatty oils very frequently calls for careful chemical investigation. The presence of soap, free fatty acids, etc., in them is of minor importance; the first, readily removable by washing with water after dissolving the oil-sample in carbon disulphide, and the second hardly to be called an adulteration, as free fat acids are normally present in many vegetable oils. The question as to whether they

are present may be settled by Jacobsen's method of adding a litt rosaniline to the oil. If free fatty acids are present, the oil turns rein color in consequence of the formation of rosaniline oleate. More in portant is the adulteration with resin and with hydrocarbon oils. the absence of free fatty acids, resin may be isolated from fixed oils I agitating the sample with moderately-strong alcohol, separating t spirituous solution and evaporating it to dryness. The separation the resin acids from free fatty acids is best effected by Twitchell method, which is based upon the fact that the fatty acids are convert into ethyl esters when acted upon by hydrochloric acid gas in the alcoholic solution, whereas colophony resin undergoes little or 1 change, abietic acid separating from the solution. For details, s Allen, Com. Org. Anal., 4th ed., ii. p. 77. Hydrocarbon oils may general be determined by saponifying the sample with alcoholic potash (fi grammes oil, two grammes caustic potash, and twenty-five cubic cenmetres ninety per cent. alcohol). The soap so obtained is mixed wi clean sand, the alcohol evaporated over the water-bath at a temperatu of not over 50° C., and the residue extracted with ether or petroleu spirit. From this solution, on evaporation of the solvent, will be gotte any hydrocarbons present.

An outline method of analyzing fatty oils containing foreign mitures, due to Allen,\* is given on the following page.

The analysis of soaps is a most important matter, as with the var ing composition of soaps, shown on page 82, a control is absolute necessary for those using or purchasing in quantity. One of the mc satisfactory schemes for a complete soap analysis is that of A. R. Leed which is given on page 93. A similar one, agreeing with that of Lee in general outlines, is given by Allen † in his excellent work on "Commercial Organic Analysis." In the water determination, great camust be taken to heat gradually at not too high a temperature at fit (40° to 50° C.), and then slowly to increase to 100°, and continue unno further loss of weight is observed.

The separation of the mixed fatty acids is usually only affected in t. mechanical way described in connection with stearic acid. (See p. 74 An exact chemical separation of these higher fatty acids is hard possible. The most satisfactory method known is that of Heintz (Jou für Prac. Chem., lxv, i), based on the fractional precipitation of the alcoholic solution of the acids with magnesium acetate. This salt precipitates acids of the stearic series more easily than it does oleic ac and its homologues, and of the different homologues of the stearic series those of the highest molecular weights are thrown down first.

Commercial glycerine is seldom free from contamination, and variety of impurities are liable to be present. The impurities of raglycerine are much greater in number and amount than those present in the distilled product, and of the former, glycerine from soap ly

<sup>\*</sup> Allen, Commercial Organic Analysis, 2d ed., ii, p. 87. † Ibid., p. 251.

# Outline Method of Analyzing Fatty Oils containing Foreign Admixtures.

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From 5 to 10 grammes weight of the sample (previously melted, if necessary) is passed through a dry filter, unless already perfectly clear.

disulphide. The squeous liquid is	repeatedly by agitation with water	solvent and heat the residual oil dd standard soda cautiously, agita-hich remains after shaking. Note the free fatty and resin acids, and any undissolved oil, dilute the alco-aroleum spirit; separate, evaporate	l off alcohol, dissolve soap in warm leparate and agitate aqueous liquid	distilled at 100°, and the last traces of the solvent removed by a current of air or other means, leaves the hydrocarbon oils in a state fit for identification and further examination.		
THE CLEAR OIL is agitated in a stoppered separator with water* and ether, or recently-distilled carbon disulphide. The aqueous liquid is separated, and the oil solution again shaken with water if the previous treatment was found to remove anything.	OIL. SOLUTION. Agitate with dilute sulphuric acid and separate.* Wash residual oil repeatedly by agitation with water the aqueous liquid no longer reddens litmus.	with alcohol and a few drops of solution of phenol-phthalen. Then add standard soda cautiously, agitating the whole, between each addition, until a pink color is obtained, which remains after shaking. Note the volume of soda solution required, as the quantity used is a measure of the fee fatty and resin acids, and will determine the necessity of looking further into their nature. Separate any undissolved oil, dilute the alcohol at a gentle heat, and agitate with petroleum spirit; separate, evaporate off separated oil to the main portion.	in ether or earbon disulphide. Distil off the reps of solution of phenol-phthalein. Then such addition, until a pink color is obtained, a required, as the quantity used is a measure of of looking further into their nature. Separat he alcohol at a gentle heat, and agitate with paracted oil to the main portion.	L in ether or earbon disulphide. Distil off drops of solution of phenol-phthalein. The each addition, until a pink color is obtained an required, as the quantity used is a measure ity of looking further into their nature. Separity of looking further into their nature. Separity of looking further into their nature.	OIL. Saponify with alcoholic potash. Boil off alcohol, dissolve soap in warm water, and agitate cooled solution with ether. Separate and agitate aqueous liquid a second and third time with ether.	AQUEOUS LIGUID  contains the glycerine and soap formed by the saponification of the neutral fixed oil of the sample. If the solution be treated with hydrochlorio acid and agitated with ether, the weight of the fatty acids left on evaporating the etheral layer, multiplied by 1.055, will give, approximately, the weight of the neutral fixed oil.
in a stoppered separator wit haken with water if the pre	OIL SOLUTION. Agitate with dilute sultill the aqueous liquid no longer reddens litmus.		AQUEOUS LIQUID. Add hydrochloric seid	and agitate with ether or carbon disulphide. Evaporate the ethereal layer at 100°, and weigh residue representing mixed free futty and riesin acida of original sample, and, if soaps of aluminum or he a vy metals were present, of the fatty acids resulting from their decomposition.		
R OIL is agitated oil solution again s	OIL SOLUT	ACID LIGUID may contain sulplates of atunt- num and heavy metals, previously existent as soaps.				
THE CLEA	AQUEOUS LIQUID	of the lightmetals, It is evaporated to dryness at 100° C, and the residue weighed and further analyzed if desired.				
RESIDUE may contain sult, curd, under, stand.	and insoluble matters generally. It may be washed	with ether, dried and we ight ed; then igniced and weighed again; the difference being the organic matter.				

f an aliquot portion of the oil solution is not blackened by sulphide of ammonium, and leaves no ash on ignition, thus proving the absence of any metallic compounds, the treatments with water and sulphuric seid may be advantageously omitted.

ſ	EXTRAOT is uncombined fat.	Dry at 110°	and weig	h.			
	two sacid resp free Call Nac						
	Sulphuric acid used cor- responds to combined soda in the soap. Calculate as Na <sub>2</sub> O.	and giyeerine. Ti mal soda solution.	nor.	II is soap (fathy rops of phenol-p			
-	After tiration evaporate to dry- ness on the water hath. Treat with absolute alcohol. Evaporate the alcoholic solution to dryness in a tared dish, and weigh as glycerine.	FILTRATE.—Combined soda and giveerine. Titrate with normal soda solution.	e excess of water and Boil, filter, and wash	anhydride, resin, and hthalein. If necess	RES		Weig
	Post, coo, and with silver nit shake well for Precipitate is stearate, palmitate, and cleate of silver.	RESIDUE 110° and weigh strong alcohol, indicator, sape	nd boil off the sash.	d combined alkal sary, titrate with	IDUE is soap a	Ŧ	Weigh out 5 grammes.
	with silver intrate by adding in fine powder and shake well for ten minutes. Allow to settle.  Precipitate is stearate, yer. Filter 50 c.c. from the total pal mit ate, 100 c.c. Decompose with 20 c.c. of HCl (1:2). Allow the silver chloride to settle and evaporate an aliquot part of the ethereal solution in a tared dish. Dry at 110° and weigh. After applying correction for oleic acid, the weight corresponds to the restn. This weight subtracted from the combined weight of fatty acid and resin gives the futty acid.	RESIDUE.—Futly acids and resin. Dry at 110° and weigh. Dissolve an aliquot part in 20 c.c. strong alcohol, and using phenol-phthalein as an indicator, saponify with soda in slight excess.	Add a large excess of water and boil off the alcohol. Decompose with excess of mal H <sub>s</sub> SO <sub>4</sub> . Boil, filter, and wash.	EXTRACT is soap (fatty anhydride, resin, and combined alkali), glycerine, and free alkali. Add two or three drops of phenol-phthalein. If necessary, titrate with normal sulphuric acid.	RESIDUE is soap and mineral constituents. Treat with alcohol	Treat with petroleum-ether.	es. Dry at 100° C. Loss corresponds to water.
	Sodium Carbonate.—Titrate with norma acid, and calculate as Na <sub>2</sub> CO <sub>3</sub> .	l sulphuric	FIL? bonate, silicate.	RES silicate, water.	n alcohol		to water.
	Sodium Ohloride.—Titrate with silver weigh as silver chloride. Calculate as NaCl.	nitrate or	TRATE chloride Divide i	SIDUE.	•		
	Sodium Sulphate. — Weigh as barium Calculate as Na <sub>2</sub> SO <sub>4</sub> .	sulphate.	FILTRATE.—Sodium car- bonate, chloride, sulphate, and silicate. Divide into 4 eq'l parts.	–Sodium ınd insol			
	Sodium Silicate.—Decompose with HCl mine the soda combined in silicate and the s	ilica.		uble res		} !	
	starch into glucose. Titrate with Fehling's solution. Subtract the weight of the starch so found, and the difference is the insoluble mineral constituents.	weight is the starch and insoluble residue.  STAROH.—Convert the	RESIDUE —Starch and insoluble residue. Dry the filter and weigh. The	RESIDUE.—Sodium carbonate, chloride, sulphate and silicate, starch, and insoluble residue. Wash with 60 c.c. of water.			

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is much more impure than the product resulting from the autoclave process. Thus the mineral matter remaining as ash in the case of a distilled glycerine never amounts to more than .2 per cent., while in raw glycerine from soap lyes the ash usually ranges from seven to fourteen per cent., and in that from the autoclave process considerably less. The ash will contain common salt, and with it may be the chlorides and sulphates of lead, iron, zinc, magnesium, and calcium. In glycerine from soap lyes, sulphates particularly are present. They may be accompanied by thiosulphates, sulphites, and sulphides resulting from the sulphuric acid saponification of fats. Such glycerines are purified only with great difficulty.

Precipitation with basic acetate of lead often serves to distinguish between a distilled and an undistilled glycerine. This treatment removes rosin, while rosin oil and free fatty acids are removed by shaking up the sample with chloroform. The direct determination of the amount of true glycerine in commercial samples can be effected with moderate accuracy by the method of oxidation with potassium permanganate in alkaline solution, whereby the glycerine is oxidized to oxalic acid, which is then determined as calcium salt. For details, the reader is referred to Allen's "Commercial Organic Analysis," 4th ed., vol. ii, p. 457.

More accurate is said to be the "acctin" method of Benedikt & Cantor, which depends upon the quantitative formation of glyceryl triacetate when glycerine is heated with acetic anhydride. It is carried out as follows: 1 to 1.5 grammes of the crude glycerine is heated with seven or eight grammes acetic anhydride and about three grammes anhydrous sodium acetate for one to one and a half hours with inverted condenser; it is allowed to cool, fifty cubic centimetres of water are added, and the heating with inverted condenser continued until it begins to boil. When the oily deposit at the bottom of the flask is dissolved the liquid is filtered from impurities, allowed to cool, phenol-phthalein added, and dilute caustic soda (about twenty grammes per litre) run in until neutrality is obtained. Care must be taken not to exceed that point, or glyceryl triacetate is easily saponified. Twenty-five cubic centimetres of strong caustic soda (about ten per cent. strength) are now added from a pipette. The mixture is then heated for fifteen minutes and the excess of alkali titrated back with normal or half-normal hydrochloric acid. The strength of the alkali used is then determined by measuring twenty-five cubic centimetres with the same pipette and titrating it with the same acid. The difference in the two titrations gives the amount of alkali consumed in saponifying the glyceryl triacetate, and from this the glycerine can be calculated.

Various methods have been proposed for the analysis of nitro-gly-cerine, based upon its decomposition by different reagents. One of the simplest and most satisfactory is that proposed by Lunge, who uses for this purpose his nitrometer. (See p. 333.) An accurately-weighed quantity, varying from .12 to .35 gramme, according to the proportion of nitro-glycerine and the capacity of the apparatus, is introduced into the cup of a nitrometer filled with mercury. About two cubic centi-

metres of concentrated sulphuric acid is then added, and when the nitro-glycerine is dissolved the solution is allowed to enter the nitroper meter through the tap. The cup is rinsed with successive portions at two cubic centimetres and one cubic centimetre of strong sulphuric acid which are allowed to enter as before, and the contents of the nitrometroper then thoroughly agitated in the usual way, and the volume of nitroper oxide evolved read off after standing about fifteen minutes. The volume of gas in cubic centimetres at the standard pressure and temper ature, multiplied by 3.37, gives the weight of nitro-glycerine in milling grammes. Hempel states that the total volume of five cubic centimetres of sulphuric acid must not be departed from; with less than that volume the reaction proceeds too slowly, and with more the results are too lover.

In the analysis of dynamite, the nitro-glycerine may be convenient determined by exhausting the dried sample with anhydrous ether, pre erably in a Soxhlet tube (see p. 86), and weighing the insoluble residu The nitro-glycerine is estimated from the loss, and, in the absence other substances soluble in ether, such as camphor, resin, etc., this is the most satisfactory way. A complete scheme for the analysis of all nitre glycerine preparations will be found in Allen, 3d ed., vol. ii, Part p. 339.

### V. Bibliography and Statistics.

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### STATISTICS.

1. OF Oils, Fats, and Waxes.—Of the production of the various vegetable and animal oils, fats, and waxes the figures are fragmentary. While they do not always give a proper view of these industries, they will suffice to indicate in a general way the degree of their development.

The figures for importations and exportations of this class of products will in many cases give a better idea of the several fat industries.

Importations of Oils, Fats, and Related Products into the United States.

	1905.	1906.	1907.
Cocoanut oil	43,773,208 lbs.	43,821,756 lbs.	35,555,603 lbs.
Value		\$2,601,665	\$2,628,016
Rape and hemp-seed oils		1,135,203 gals.	806,033 gals.
value		\$383,775	\$405,575
Olive oil (salad)		1,812,412 gals.	3,389,516 gals.
Value	\$1,836,942	\$2,113,872	\$2,724,500

### Importations of Oils, Fats, and Related Products into the United States.

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	1905.	1906.	1907.
Olive oil (not salad)		2,538,038 gals.	1,845,701 gals.
. Value	\$757,119	\$1,106,142	\$794,574
Palm oil	19,873,557 lbs.	23,475,595 lbs.	29,475,595 lbs.
Value	\$1,081,013	\$1,296,182	\$1,888,660
Sesame oil	1,394,975 lbs.	1,354,456 lbs.	1,600,410 lbs.
Value	\$91,314	\$108,690	\$121,607
Cocoa butter	2,732,897 lbs.	3,350,025 lbs.	4,418,839 lbs.
Value	\$615,991	\$818,847	\$1,226,504
Beeswax	374,219 lbs.	585,636 lbs.	918,995 lbs.
Value	\$101,131	\$168,015	\$265,172
Soap, castile	4,588,531 lbs.	4,693,717 lbs.	5,153,565 lbs.
Value	\$294,540	\$304,818	\$346,383
Soap, toilet	1,013,651 lbs.	1,115,000 lbs.	1,207,307 lbs.
Value	\$446,526	\$477,891	\$520,600
Glycerine, crude	26,248,514 lbs.	33,276,728 lbs.	37,136,812 lbs.
Value	\$1,960,538	\$2,228,956	\$2,375,764
		(Oil Paint and T	Ima Reporter 1

### (Oil, Paint and Drug Reporter.)

### Exportations of Oil, Fats, and Related Products from the United States.

1905.	1906.	1907.
Corn oil 3,108,917 gals.	3,833,251 gals.	3,041,269 gals.
Value \$890,937	\$1,172,206	\$1,083,929
Cotton-seed oil 51,535,580 gals.	43,793,519 gals.	41,880,304 gals.
Value\$15,125,802	\$13,673,370	\$17,074,403
Cotton-seed 21,101,129 lbs.	23,717,326 lbs.	17,628,111 lbs.
Value \$235,833	\$268,330	\$209,493
Flax-seed	5,988,519 bush.	6,336,310 bush.
Value \$1,738	\$7,495,748	\$7,990,383
Soap, toilet, value \$888,838	\$1,082,893	\$1,144,879
Soaps, other 45,321,281 lbs.	42,410,534 lbs.	65,183,460 lbs.
Value \$1,781,893	\$1,698,286	\$2,661,218
Tallow 63,536,992 lbs.	97,567,156 lbs.	127,857,739 lbs.
Value \$3,022,173	\$4,791,025	\$7,182,688
Lard	741,516,886 lbs.	627,559,660 lbs.
Value\$47,243,181	\$60,132,091	\$57,497,980 °
Lard, compound, etc \$3,613,235	\$4,154,183	\$6,166,910
Candles 8,793,502 lbs.	7,972,871 lbs.	5,203,736 lbs.
Value \$701,357	\$609,188	\$473,235
Corn-cake 24,171,127 lbs.	48,420,942 lbs.	56,808,972 lbs.
Value \$278,526	\$605,34 <b>6</b>	\$677,156
Cotton-seed cake1,251,907,996 lbs.	1,110,834,678 lbs.	1,340,967,136 lbs.
Value\$13,897,178	\$13,073,150	\$17,062,594
Linseed cake	758,916,364 lbs.	665,936,164 lbs.
Value \$7,600,907	\$10,313,118	\$8,675,877
	(Oil Dointond	D

(Oil, Paint and Drug Reporter.)

### Statistics of English Trade in Oils, Fats, and Related Products.

	1900.	1901.	1902.
Imports	£40,929,185	£43,874,659	£46,953,142
Exports	4,804,370	5,032,143	5,501,008
Less re-exports	£3,861,132	£3,285,252	£2,984,592
	£41,782,223	£45,621,550	£49,469,558

(Lewkowitsch-Lect. before Society of Arts.)

Statistics of German Importations of Fats and Fatty Oits in 1905.

Value in marks.	Value in ma		
Lard 86,100,000	Beeswax 7,400,000		
Butter 71,800,000	Vegetable wax 1,700,000		
Oleomargarine 22,600,000	Linseed 68,600,000		
Cotton-seed oil 17,300,000	Palm nut and copra 60,300,000		
Tallow (beef and mutton) 15,000,000	Oil cake 51,000,000		
Fish oil 5,600,000	Rape seed 31,700,000		
Olive oil 4,900,000	Sesame seed 12,100,000		
Palm oil 3,600,000	Poppy seed 8,300,000		
Linseed oil 900,000	Earth-nuts 4,600,000		

Cocoa-nut Oil.—The annual yield of nuts in Ceylon may be taken at 1,100,000,000. In 1898 the exports of cocoa-nut oil from this island amounted to 435,000 hundredweight, and in 1899 to 400,000 hundredweight, besides large quantities of "copra" (the dried pulp of the cocoanut) and cocoa-nuts. Large amounts are also exported from the Eastern Archipelago, from British India, and from the Pacific Islands. The nuts are also exported from the West Indies, from Central America, and from Brazil.

Palm Oil.—The exportation of palm nuts from Southern Africa, according to Dr. von Scherzer, reaches 1,300,000 metric centners annually, of which the greater part goes to France. The exportation of nuts from British India, Siam, Cochin-China, China, South-Sea Islands, and Brazil together amounts to 600,000 metric centners.

Olive oil is produced chiefly in Mediterranean lands and in the East. The area under olive culture in Italy is now 2,258,000 acres. production of 1905-06 was stated to have been 3,400,000 hectolitres. while that of 1906-7 was but 1,800,000 hectolitres. The export of olive oil from Italy ranges from 50,000,000 kilos, to 92,000,000 annually, according to the crop of olives (Simmond's Tropical Agriculture, p. 394). Spain has some 2,500,000 acres devoted to olive culture, and the average annual production of oil for the last five years has been 2,976,384 metric centners. Of this the home consumption, for food, lighting, soap-making. etc., took 2,754,064 metric centners, leaving 222,320 metric centners for export. France had, a few years ago, 317,800 acres of olives under cultivation, producing 7,318,352 bushels of fruit and 392,618 hundredweight of oil. The total Greek production in 1907 was 564,761 metric tons of oil. The Algerian production was 55,239,000 kilos. of fruit, yielding 1,543,400 hectolitres (of twenty-two gallons) of oil. The exportation of Turkey and the Turkish provinces is estimated at 900,000 metric centners annually. (Heinzerling.)

The production of olive oil in California was stated at the tariff hearings in 1908 to be 350,000 gallons annually.

Rape or colza oil is cultivated in Germany, France, Austria, Hungary, Russia, Rumania, and India. The area in Germany planted with the different varieties of brassica amounted in 1882 to 445,000 acres, the crop of rape seed to 1,882,000 metric centners, valued at 50,500,000 marks.

### BIBLIOGRAPHY AND STATISTICS

England imports some 800,000 metric centners of rape seed annually, and produces quite an amount. Austria presses for oil about 550,000 metric centners of rape seed annually, obtaining 200,000 to 225,000 metric centners of oil. The total consumption of rape and rollar oil in Europe is estimated at 2,800,000 to 3,000,000 metric centhers per annum, valued at 170,000,000 to 175,000,000 marks. (Heinzerling.)

The exportation of rape seed from Russia in 1879 amounted to 1,294,-728 bushels, and from Roumanian ports, on the Danube, in 1878, to 938,376 bushels.

Sesame Oil.—The seeds come chiefly from the East Indies and the Levant, and the oil is pressed in Marseilles and Trieste. British India exported in 1885, 2,646,484 hundredweight; in 1886, 1,759,343 hundredweight; and in 1887, 2,121,119 hundredweight. France imports somewhat more than 1,000,000 metric centners; England, 250,000 metric centners; Italy, 150,000 metric centners; and Germany, 140,000 metric centners of sesame seeds.

Ground-nut Oil.—The ground-nut (pea-nut), while indigenous to America, is now cultivated, for the oil it contains, in Africa, India, the West Indies, and Brazil. The American production, located chiefly in the States of North Carolina, Virginia, Tennessee, amounts to an average of 3,500,000 bushels, or 77,000,000 pounds. The production of 1899 exceeded the average, amounting to 4,500,000 bushels. The average production of "Spanish pea-nuts" in the United States amounts to 16,500,000 pounds. About 400,000,000 pounds are annually exported from India and Africa, of which about half goes to Marseilles to be expressed for oil.

It is estimated that 3,250,000 bushels are annually eaten in the United States.

Cotton-seed Oil.—The growth of the cotton-seed industry in the United States as shown by the Census Report of 1905 has been very great. This is illustrated by the following figures:

	1890.	1900.	1905.
Value of materials	\$14,363,126	\$45,165,823	\$80,039,963
Value of products	19.335.947	58,726,632	96.407.621

The amount of cotton-seed crushed increased from 2,479,386 tons in 1900 to 3,345,370 tons in 1905.

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In 1905, one ton of cotton-seed yielded on an average 40 gallons crude oil (300 pounds), 813 pounds meal, 725 pounds hulls, 35 pounds linters and 127 pounds of waste.

Of this annual production of crude cotton-seed oil, perhaps one-fourth goes into the production of "compound lard," and the rest is partly exported as cotton-seed oil, partly used in admixture with drying oils, and partly as soap-stock.

In Europe, England is the chief country extracting the oil from the cotton-seed, which comes chiefly from Egypt. The imports of seeds into England for 1886 were 25,701 tons; for 1887, 276,570 tons; for 1888, 255,500 tons.

Hemp-seed oil is produced chiefly in Russia. The exports of hemp seed from Riga in 1878 were 629,520 bushels, and in 1879, 725,809 poods (of thirty-six pounds) of seed and 573 poods of the oil. (Spon's "Encyclopedia.")

Linseed Oil.—The supplies of linseed oil come from all countries, but most largely from Russia, the United States, and Argentina. The world's crop of linseed in recent years has been as follows:

	1903. Bushels.	1904. Bushels.	1905. Bushels.
United States	27,301,000	23,401,000	28,478,000
Canada and Mexico	957,000	843,000	907,000
Argentina	30,076,000	36,912,000	29,133,000
Uruguay	8,176,000	5,530,000	6,000,000
Austria-Hungary	1,442,000	1,380,000	1,592,000
Russia	19,544,000	20,190,000	18,900,000
Other European countries	3,631,000	1,609,000	1,666,000
India	19,263,000	22,873,000	13,856,000
Miscellaneous	65,000	36,000	35,000
Total1	10,455,000	112,774,000	100,607,000

(Year Book of Agriculture, U.S., 1906.)

### Cocoa Product of the World.

	1904. Pounds.	1905. Pounds.	1906. Pounds.
St. Thomas	45,252,000	55,952,000	51,800,000
Ecuador	62,685,000	46,579,000	54,900,000
Brazil	51,059,000	46,496,000	60,400,000
Trinidad	40,949,000	44,133,000	35,100,000
Santo Domingo	29,890,000	28,185,000	30,200,000
Venezuela	28,768,000	25,795,000	24,300,000
Gold Coast (Lagas)	12,540,000	12,491,000	13,400,000
Grenada	13,727,000	12,028,000	10,400,000
Other countries,	38,223,000	40,015,000	46,200,000
•	323,093,000	311,674,000	326,000,000

Fish Oils.—The amounts of sperm, whale, and fish oils of all kinds obtained annually, according to Mulhall,\* are: sperm and whale oil, 1,485 000 hectolitres (32,670,000 gallons); fish oils of other kinds, 1,170,000 hectolitres (25,740,000 gallons), and oil from sea-birds 58,500 hectolitres (1,270,000 gallons).

The value of the fish oils exported from Newfoundland in recent years is given as follows:

	1906.	1907.
Cod-liver oil, crude	\$354,352	\$358,713
Cod-liver oil, refined	34,995	31,735
Seal oil	297,430	447,967
Whale oil	222,761	173,011

<sup>\*</sup> Mulhall, Production and Consumption, p. 142.

The Norwegian cod-liver oil production from the three districts Lofoten, Romsdal, and Lodde is thus given on the authority of F. Möller (Cod-liver Oil and Chemistry, London, 1895):

YEAR.	Number of fish.	Barrels of com- mon liver oil.	Barrels of steam- prepared liver oil	
1890	51,614,000	58,535	21,178	
	40,880,000	88,815	22,881	
	44,212,000	47,051	16,831	
	47,738,000	41,851	18,757	
	52,484,000	84,670	21,294	

The production of Norway in recent years is given as follows: 1 1905, 42,000 hectolitres; in 1907, 46,809 hectolitres.

The value of the cod-liver oil exported from Norway is thus given:

1906. Kronen. 5,519,000 1907. Kronen. 4,724,900

Spermaceti and Sperm Oil.—The production of spermaceti in the American whale-fisheries was 1,300,959 gallons in 1878, and 1,285,45 gallons in 1879. The exports of sperm oil from New York in 1878 were 912,603 gallons, and in 1879, 1,089,137 gallons. (Spon's "Encyclopedia.")

Lard and Lard Oil.—The production of lard in the United State during recent years is thus given by the Cincinnati Price Current:

Of this production from one-third to one-half is "compound lard, or lard admixed with cotton-seed oil and beef stearine.

Tallow.—The production of tallow for all European countries for the year 1882, according to Mulhall,\* amounted to 355,700 tons, for the United States to 330,000 tons, and all other countries, 60,000 tons, making a total of 745,700 tons. The exportations of Russian tallow has greatly diminished in recent years; they were 40,300 tons in 1860, 21 100 tons in 1870, and 10,400 tons in 1880. The exportations from the United States, River Plate in South America, and Australia, on the other hand, have increased, especially the first and the last of these. In the year 1883 the exportations of tallow were as follows: From the Unite States, 45,000 tons; from Australia, 28,000 tons; from Argentine Republic, 10,500 tons, and from Uruguay, 12,000 tons. (Heinzerling.)

Wool Fat.—In 1899, 1,038,000 tons of raw wool were worked for the extraction of the wool fat (Donath and Margosches, Vorträge.)

Chinese or Insect Wax.—The amount annually produced is value by Professor Thistleton Dyer, of Kew Gardens, England, at £600,00

<sup>\*</sup> Mulhall, Dictionary of Statistics, p. 434.

Carnauba Wax.—The exportations of this wax from Brazil in recent years were as follows:

190	L. 1902.	1903.	1904.
Quantity in tons 997	7 1926	1897	2559
Value in milreis 1044	L 2662	3291	6316
Value in marks 996	2562	4239	8567

Japan Wax.—The exportations from Japan were in 1906 2,348,175 kilos., valued at \$970,092.

Soaps.—The production of the United Kingdom for 1907 was as follows: Soap, 737,500,000 lbs., valued at \$40,933,600; candles, 102,617,000 lbs., valued at \$8,044,800. In 1909 the Census Bureau reported the production of soaps of all kinds in the United States as 1,388,972,065 lbs., valued at \$57,358,431.

Candles.—Price's Patent Candle Co. of England manufacture yearly 7000 tons of paraffin candles and 3000 tons of stearine candles. The Saxon paraffin works manufacture yearly 6750 tons of paraffin and composition candles.

Glycerine.—The total output of crude glycerine in the world has been stated to be 40,000 tons per annum, of which 14,000 tons are obtained in soap manufacture and 26,000 tons in stearine manufacture. The glycerine from these two sources is produced as follows:

•		soap- ing.	From stearic acid manufacture.
England	5500	tons.	1200 tons.
France	3500	"	6000 "
Germany	2000	**	3000 "
United States	3000	66	3000 "
Holland		"	2000 "
Austria		"	2000 "
Russia		**	2000 "
Belgium		66	1800 "
Italy		66	1800 "
Spain		"	1500 "
Other countries		"	1700 "

The development of the glycerine and nitro-glycerine production in the United States has been shown in the Census Report of 1905:

	1900.		1905.	
Production of glycerine	15,383,778	lbs.	19,311,997	lbs.
Value	\$1,893,886		\$2,397,205	
Production of nitro-glycerine	35,280,498	lbs.	51,579,270	lbs.
Value	\$5,532,570		\$7,730,175	
Production of dynamite		tons	65,460	tons
Value	\$8,247,223		\$12,900,193	

# CHAPTER III.

#### INDUSTRY OF THE ESSENTIAL OILS AND RESINS.

# I. Raw Materials.

1. ESSENTIAL OILS.—The essential or volatile oils, as they are termed, are found extensively distributed throughout the vegetable kingdom. They occur in almost all parts of the plants except the cotyledons of the seeds, in which, in general, the fixed or fatty oils are contained. The essential oils impart the peculiar and characteristic odors to the plants; they furnish us our perfumes, spices, and aromatics, and many of them possess valuable medicinal properties.

The essential or volatile vegetable oils are procured in several ways: (1) by distillation; (2) by absorption or "enfleurage"; (3) by means of solvents: (4) by expression; and (5) by maceration.

In the distillation method the plants are put into the still along with about an equal weight of water, either with or without previous soaking, and the distillation carried on rapidly. If necessary, the water that separates from the oil in the receiver is returned to the still and driven over a second or third time. The separation of the oil and water is effected in what is termed a "Florentine receiver," from the bottom of which the water can be siphoned off without disturbing the oily layer. The odors of some flowers, such as jessamine and mignonette, are too delicate to bear heat, and for these the process of absorption, or "enfleurage," as it is called in the south of France, is employed. Sheets of glass in wooden frames, called chassis, are coated in their upper and lower surfaces with grease about a tenth of an inch in thickness. The flowers are spread upon this grease, and a number of frames are superimposed one upon another. After a day or two the flowers are carefully removed and replaced by fresh ones, and this is continued for two or three months, till the fat is impregnated with the odors. It is then removed and extracted with alcohol. Recently the grease has been replaced in some cases by soft paraffin, glycerine, or vaseline.

For the extraction by solvents, light petroleum ether, carbon disulphide, and latterly carbon tetrachloride are employed, and the solvent recovered by distillation. The essential oils of lemons and oranges of commerce, and some other fruits, are chiefly obtained by submitting the rind to powerful pressure. The oils are more fragrant but not so white as when distilled, and the process is only adapted for substances which are very rich in essential oils. Flowers with very delicate perfume, such as those of the bitter orange, violets, etc., which would be spoiled by distillation, are treated by maceration. The medium used for infusion is clarified beef or mutton suet or lard. The fat is melted,

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the flowers immersed, and the mixture stirred occasionally for a day or so. The exhausted flowers are removed and fresh ones introduced, and such renewals are continued till it is judged that the fat is sufficiently charged with the oil.

The essential oils are usually more limpid and less unctuous than the fixed oils, but some of them, when in the crude state, may be quite thick or even semi-solid from admixtures of solid and crystalline ingredients with the more liquid portion. Their odor is that of the plants which yield them, and is usually powerful; their taste is pungent and burning. They mix in all proportions with the fixed oils, dissolve in both alcohol and ether, and are sparingly soluble in water, forming "perfumed" or "medicated water." They are not saponifiable. Their boiling-points usually range from 310° to 325° F. (154.5° to 162.7° C.), although in some oils the hydrocarbons boil at 356° F. (180° C.) or even higher. They are, however, capable in most cases of being distilled in a current of steam. In specific gravity they vary from oil of citron .850 to oil of wintergreen 1.185 at 15° C.

Chemically, essential oils are in the main mixtures of a class of hydrocarbons known as terpenes and oxygen-containing substances, such as alcohols, esters, ketones, aldehydes, and phenols. These oxygenated bodies when solid have been termed camphors.

- I. The oils which do not contain oxygen are composed of hydrocarbons of what is called the *terpene* series. These seem to be of a common formula, which is  $C_{10}H_{16}$  or a multiple of this. We may distinguish several groups.
- 1. Hemiterpenes, C<sub>5</sub>H<sub>8</sub>.—A hydrocarbon of this formula is yielded when caoutchouc is destructively distilled.
- 2. Terpenes, C<sub>10</sub>H<sub>10</sub>.—The true terpenes. Of these some six or eight distinct compounds have been obtained, but they may exist in different physical modifications according as they are right or left rotatory or inactive to polarized light.
- 3. Sesquiterpenes,  $C_{15}H_{24}$ .—This group includes the hydrocarbons of oils of cedar, cubebs, and cloves.
- 4. Diterpenes, C<sub>20</sub>H<sub>32</sub>, include colophene, obtained in the treatment of oil of turpentine, and possibly others.
- 5. Polyterpenes,  $(C_{10}H_{10})_n$ , include the polymerized hydrocarbons of caoutchouc and gutta-percha.
- II. The oils which contain oxygen may owe this to one of several classes of oxygen compounds.
- 1. Camphors.—This group includes common or Japan camphor, borneol, cineol, or eucalyptol, menthol. These bodies are either alcohols or ketones in chemical character.
- 2. Unsaturated Alcohols and Aldehydes.—A number of compounds of this class have recently been identified as constituting important odoriferous principles in oils. Thus, geraniol, or rhodinol and linalool (coriandrol) are unsaturated alcohols, while eitral and citronellal are insaturated alchydes.
  - 3. Esters or Compound Ethers of Alcohols.-The formic, acetic, and

valeric ethers of borneol and the formic and acetic ethers of linalo and geraniol are all found natural in essential oils. Methyl salicyla is another compound ether, constituting the main constituent of oil a wintergreen.

- 4. Phenols.—Thymol, of oil of thyme, and carvacrol, of origanum of belong to this class.
- 5. Ethers of the Phenols.—Anethol, of anise oil, eugenol, of oil cloves, and safrol, of oil of sassafras, belong here.
- 6. Aromatic Aldehydes.—Benzaldehyde, salicyl aldehyde, anisic ald hyde, vanillin, cumin aldehyde, and cinnamic aldehyde belong to the class.
  - III. The oils which contain sulphur seem to belong to two classes.
- 1. Sulphides of Organic Radicals.—Garlic oil, onion oil, leek oil, an similar oils contain allyl and vinyl sulphides.
- 2. Sulphocyanates of Organic Radicals.—Mustard oil and some other contain allyl sulphocyanate.

Oil of Turpentine.—This oil is produced by all the Conifera i greater or less amount. It flows from cuts in the tree as a balsam (se p. 107), known as turpentine. This, on distillation with steam, yields the volatile oil of turpentine, and there remains behind the resin (colphony resin) commonly known as "rosin." While a number of mine varieties of turpentine are known, such as Venetian, Hungarian, Stra burg, Chios turpentines, and Canada balsam, which are of pharm ceutical value, but three commercially important varieties of oil of tu pentine need to be noted. They are English or American oil of tu pentine, from Pinus australis and Pinus tæda, collected in North ar South Carolina and Georgia; the French oil of turpentine from Pina maritima, collected in the neighborhood of Bordeaux; and the Russia or German oil of turpentine, from Pinus sylvestris. Of the America oil, only seventeen per cent. is obtained on distillation of the crue turpentine balsam; of the French, as much as twenty-five per cent. oil may be obtained; and of the Russian, thirty-two per cent. essential composition of all three of these oils, when rectified, is C<sub>10</sub>H but distinct hydrocarbons, differing in physical if not in chemic characters, are considered to be present in each of the three oils. The the terpene, C<sub>10</sub>H<sub>16</sub>, of French oil of turpentine is lavo-rotatory, and known as lævo-pinene, while that of the American oil is dextro-rotator and is known as dextro-pinene. Otherwise they are practically identic in properties. Russian oil of turpentine consists mainly of a hydroca bon, sulvestrene, which boils some sixteen to twenty degrees Centigrae higher than the others, and shows some other minor differences. T commercial oil of turpentine is a colorless, very mobile, highly refractive liquid, of pleasant odor when freshly rectified, but becoming disagre able by exposure to the air, as it absorbs oxygen and becomes resinor It is almost wholly insoluble in water, glycerine, and dilute alkali: and acid solutions. It is soluble in absolute alcohol, ether, carbon dist phide, benzene, petroleum spirit, fixed and essential oils. It is itself solvent for sulphur, phosphorus, resins, fats, waxes, caoutchouc, etc.

Within recent years a product known as "wood turpentine" has been obtained extensively through the Southern United States by distilling pine wood stumps and logs with steam. While resembling the genuine spirits of turpentine, it is inferior in some respects, as it is of different constitution in part.

Turpentine yields a number of interesting and medicinally important derivatives under the influence of different reagents. Thus, by the action of hydrochloric acid gas is formed pinene hydrochloride,  $C_{10}H_{17}Cl$ , known as "artificial camphor." When turpentine oil stands in contact with water, especially in the presence of nitric acid and alcohol, it unites with three molecules of water to form a hydrate,  $C_{10}H_{18}(OH)_2 + H_2O$ , known as terpin hydrate. When the anhydrous terpin,  $C_{10}H_{18}$  (OH)<sub>2</sub>, is distilled with dilute sulphuric acid it loses a molecule of water and yields terpineol,  $C_{10}H_{17}(OH)$ , an oil of hyacinthine odor which is used in medicine. When sulphuric acid is allowed to stand in contact with oil of turpentine and the mixture after a day's standing is heated to boiling, the oil is changed into an optically inactive mixture of terpenes, known as terebene, which boils at  $156^{\circ}-160^{\circ}$ .

Camphor.—This is one of the most important of the oxidized principles which were referred to as accompanying the hydrocarbons in the crude essential oils. While the name is frequently used to designate a class of compounds, it is commercially restricted to the laurel camphor,  $C_{10}H_{10}O$ , which is obtained from the wood of the Japan camphor-tree (Camphora officinarum) by distillation with water and after purification with sublimation. It forms a colorless, translucent, tough, fibrous mass, but may be obtained crystallized in prisms. It has a peculiar, fragrant odor and burning taste. It melts at 347° F. (175° C.), and boils at 399.2° F. (204° C.). It is nearly insoluble in water, but readily soluble in alcohol, ether, acetone, carbon disulphide, chloroform, and oils.

Camphor has also been obtained on a commercial scale within a few years from oil of turpentine. By the action of anhydrous oxalic acid upon the turpentine is formed pinyl oxalate and pinyl formate. By distillation with steam in the presence of an alkali, the pinyl oxalate is converted into camphor, while the formate is changed into borneol. The white pulverulent mixture of the two is at once submitted to oxidation to change the borneol into camphor. The yield in camphor is at present from twenty to thirty per cent. of the turpentine used.

Borneol (or Borneo camphor), cineol (or eucalyptol), linalool, and geraniol are camphors with the formula  $C_{10}H_{18}O$ . They occur either free or in the form of esters in many of the essential oils.

Menthol, C<sub>10</sub>H<sub>20</sub>O, is a white, camphor-like body found in peppermint oil, from which it may be chilled out. It is largely used in medicine and pharmacy.

Thymol, C<sub>10</sub>H<sub>14</sub>O, found in a number of essential oils, is a solid phenol.

2. RESINS.—The resins are products of the oxidation of the terpenes, and either accompany them in the crude essential oils or occur as exuda-

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tions from trees hardening on exposure to the air. The chief consti uents of the resins are resin esters, resin acids, and a neutral class know as resenes, of which latter little is known. The resin esters contain peculiar alcohols, the resinols, which are colorless, and resino-tannoi which are colored, and give the tannin reaction. The classification resins usually adopted at present is into (1) true resins, (2) gu resins, and (3) oleo-resins or balsams. The true resins are hard, cor pact products of oxidation, made up chiefly of what are termed "res acids," which, admixed with fatty acids, are capable of saponifyir with alkalies and yield "rosin soaps" (see p. 70); the gum resins diffe from the true resins only in containing some gum capable of softenir in water; and the oleo-resins include the mixtures of essential oil ar resin of whatever consistency and the mixtures of benzoic and cinnam acid and salts of these acids. This last is obviously much the largest the three. To the first class belong the hard resins, which serve for tl manufacture of varnishes, such as copal, dammar, mastic, sandarac dragon's blood, gum lac, and amber; to the second class, olibanum frankincense, myrrh, ammoniacum, asafætida, galbanum, and trag canth; and to the third class, crude turpentine, benzoin, storax, copaib Peru and Tolu balsams. Brief mention will be made of a few of tl commercially more important.

Amber is a fossil resin found in detached pieces on the sea-coas and particularly in the blue earth along the Baltic coast of Prussia, b tween Königsberg and Memel. Its applications are chiefly as an artic for the manufacture of mouth-pieces of pipes and cigar-holders and for the preparation of a superior varnish, and for the productic of amber oil and succinic acid.

Gum Arabic.—This is included among gum resins because an exud tion analogous to other resins, but is almost wholly a gum, soluble water, and closely related chemically to the starch group. (See p. 185 It is yielded by the different species of Acacia, and, at present, com chiefly from Central and North Africa, by the way of Egypt, Senegand the Red Sea. It varies greatly in purity and color, and is use because of its mucilaginous character, for a multitude of application as in medicine, confectionery, preparation of textile fabrics, manufature of inks, etc.

Copal and Animé.—These terms include a number of related resir which are of both fossil and recent origin. The Zanzibar copal or anin is chiefly fossil, and is dug out of the soil by the natives for some distance along the southeastern coast of Africa. Some freshly-exude copal resin is also gathered here. On the west coast of Africa, for distance of seven hundred miles, copal resin is also dug as a foss. When of good quality it is too hard to be scratched by the nail, has conchoidal fracture, and a specific gravity ranging from 1.059 to 1.08. Unlike others, the copal resins are soluble with difficulty in alcohol ar essential oils, and this property, combined with their extreme hardner renders them very valuable for making varnishes.

Dammar is obtained from the Dammara orientalis, a coniferous tre

indigenous in the East Indies and Moluccas, and also from Dammara australis, in New Zealand. The two varieties are known as East Indian and Australian dammar, the latter being also known as Kauri resin. The former is that commonly met with in commerce under the simple name of dammar. The resin occurs in masses, coated on the exterior with white powder from mutual attrition, while the interior is pale amber-colored and transparent. It is scratched by copal, but is harder than rosin. The resin splits and cracks at the temperature of the hand. The Kauri variety is chiefly fossil in its origin. The dammar is extensively used in the manufacture of varnishes.

Lac is a resinous incrustation produced on the bark of the twigs and branches of various tropical trees, by the puncture of the female "lac insect" (Coccus lacca). This crude exudation constitutes the stick-lac of commerce. Shell-lac or shellac is prepared by spreading the resin into thin plates after being melted and strained. In the preparation of the shellac, the resin is freed from the coloring matter, which is formed into cakes, and is known as "lac-dye." "Button-lac" differs from shellac only in form. Instead of being drawn over a cylinder, the melted lac is allowed to fall upon a flat surface, and assumes the shape of large cakes about three inches in diameter and one-sixth inch thick. Bleached lac is prepared by dissolving lac in a boiling lye of pearl-ash or caustic potash, filtering and passing chlorine through the solution until all the lac is precipitated. This is then collected, well washed, and pulled in hot water, and finally twisted into sticks and thrown into cold water to harden.

Seed-lac is the residue obtained after dissolving out most of the coloring matter contained in the resin. The common shellac is used in varnishes, lacquers, and sealing-wax; the bleached lac in pale varnishes and light-colored sealing-wax.

Mastic is the resin flowing from the incised bark of the Pistacia lentiscus, and comes exclusively from the Island of Chios, in the Mediterranean. It comes into commerce in pale, yellowish, transparent tears, which are brittle, with conchoidal fracture, balsamic odor, and softens between the teeth. It is soluble in alcohol, oil of turpetine, and acetone. It is used in varnish-making.

Colophony Resin (rosin) is the solid residue left on distilling off the volatile oil from the crude turpentine. The resins from the Bordeaux turpentine and that from the American turpentine are substantially identical. Rosin is a brittle, tasteless, very friable solid, of smooth, shining fracture, specific gravity about 1.08. It softens at 80° C. (176° F.), and fuses completely to a limpid yellow liquid at 135° C. (275° F.).

It is insoluble in water, difficultly soluble in alcohol, but freely soluble in ether, acetone, benzene, and fatty oils. With boiling alkalies it takes up water to form abietic acid, and then unites with the alkali to form a rosin soap. (See p. 70.)

3. CAOUTCHOUC (India-rubber).—This is the chief substance contained in the milky juice which exudes when a number of tropical trees belonging to the natural orders *Euphorbiacew*, *Artocarpacew*, and *Apo-*

cynaceæ are cut. This juice is a vegetable emulsion, the caoutchouc king suspended in it in the form of minute transparent globules. The emulsion is easily coagulated, and the caoutchouc caused to separa by the addition of alum, salt solutions, and other means.

Caoutchouc belongs in the same general category as the essential oil as its chief constituent is polyprene  $(C_5H_8)_n$ . This is a polymer of is prene  $(C_5H_8)$ , which latter along with dipentene or caoutchene  $(C_{10}H_{10})$  is obtained when caoutchouc is destructively distilled.

The different species of rubber-trees are cultivated in Mexico, Sout America, and the West Indies, in the East Indies, Borneo, Sumatra, and the African coast.

The commercial varieties of caoutchouc may be grouped under for heads, the relative value of which accords with the order in which the are placed: South American: Para, Ceará, Carthagena, Guayaquil; Ceatral American: West Indian, Guatemala; African: Madagascar, Mozan bique, West African; Asiatic: Assam, Borneo, Rangoon, Singapor Penang, and Java. The Para rubber (from the Hevea Brasiliensis of Siphonia elastica) is the best of the many varieties, and commands the highest price.

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Caoutchouc, when pure, is nearly white, but the commercial varieties are discolored by smoke in the drying of the freshly-exuded juice in th methods usually followed. At ordinary temperatures caoutchouc is sof elastic, and so glutinous that two freshly-cut surfaces pressed strongl together will permanently adhere. At low temperatures it is harder, less elastic and adhesive, while, on heating it, the elastic property dis appears also, and it becomes perfectly soft and can be kneaded. water caoutchouc swells up without dissolving; in ether, petroleun naphtha, benzene, carbon disulphide, oil of turpentine, rosin oil, and oi gotten by the dry distillation of the rubber itself, the caoutchouc swell up rapidly, and after a time dissolves to a greater or less degree. best solvents are carbon disulphide, chloroform, and carbon tetrachle ride, and Paven recommends carbon disulphide, to which five per cen of absolute alcohol has been added, as excellent. Caoutchouc is quit indifferent to most chemical reagents, but is attacked by strong nitri and sulphuric acids. Fatty matters present in the solvents used seem t have a deleterious action upon the caoutchouc, causing it to become first soft and afterwards hard and brittle. Caoutchouc softens at 120° C melts at about 150° C., and decomposes at 200° C.

Highly purified rubber has a specific gravity of 0.911 at 17° C., an the technically pure substance from .915 to 0.931. On exposure to ai and light, rubber is oxidized to a hard resin somewhat resembling she lac. Hence articles of caoutchouc should preferably be preserved in the dark in well-closed containers. If they become hard, their elasticity may be restored by exposing them to the vapor of carbon disulphide and subsequently of petroleum.

Chlorine and bromine act energetically on caoutchouc to form bot addition and substitution compounds. Strong sulphuric acid chars an oxidizes caoutchouc on heating, and nitric acid converts it gradually o boiling into oxalic, camphoric, and camphoronic acids. Ozone also attacks it readily, producing a viscid oil. Nitrogen tetroxide as dry gas passing into caoutchouc in benzene solution forms a compound  $C_{10}H_{10}N_2O_4$ , which is readily soluble in acetone but almost insoluble in methyl and ethyl alcohols, ether, chloroform, and carbon disulphide. This reaction is used, therefore, for the determination of real caoutchouc in manufactured rubber.

4. GUTTA-PERCHA AND SIMILAR PRODUCTS.—Gutta-percha is obtained from the milky juice of different trees of the genus Isonandra, belonging to the natural order Sapotacex. By the coagulation of the collected juice the gutta-percha globules mass together and can be kneaded into lumps. The localities in which the gutta-percha is cultivated are Borneo, Sumatra, and the Malayan Archipelago. It comes into commerce in irregularly- and fancifully-formed blocks. It forms a fibrous mass, varying in color from nearly white to reddish or brownish, looking something like leather clippings cemented together, and has a specific gravity of .979. At ordinary temperatures it is hard and somewhat elastic, at 25° C. (77° F.) it becomes soft, and at 50° C. (122° F.) it can be kneaded or rolled out into plates. Between 55° C. and 60° C. it is so thoroughly plastic as to be drawn into tubes, thread, plates, and at 120° C. (248° F.) it melts. Its elasticity seems distinctly greater in the direction of its fibre than in an opposite one, while caoutchouc is equally elastic in all directions. Gutta-percha is a poorer conductor of electricity than caoutchouc, and hence its extensive use in insulating wires and cables. Its power of softening at 45° C. is partly overcome by the process of vulcanization or union with sulphur. Chemically, guttapercha seems to be composed, like caoutchouc, of a hydrocarbon  $(C_{10}H_{16})_n$ , but is always accompanied by a certain amount of oxidation Payen found that the crude gutta-percha, after thorough exhaustion with alcohol, left seventy-eight to eighty-two per cent, of a pure hydrocarbon, that he termed gutta, which, at from 15° C. to 30° C. (59° to 86° F.), was tenacious and ductile, but not very plastic.

Gutta-percha dissolves in all the solvents of India rubber. It is also attacked readily by ozone, but not at all by hydrofluoric acid, which is, therefore, often kept as a reagent in bottles of gutta-percha. Nitrous acid gas  $N_2O_3$  acts upon it as upon caoutchouc, giving rise to a nitrosite  $C_{10}H_{16}N_3O_7$ .

Balata is the dried, milky juice of the bully-tree (Sapota Milleri), which flourishes in Guiana. The balata is obtained from the juice in a manner similar to gutta-percha. In its properties it is intermediate to caoutchouc and gutta-percha; it is more plastic and readily kneaded than the former and more elastic than the latter. At ordinary temperatures it is compact and horny, but at 49° C. already it becomes soft, and can be shaped. Towards solvents it behaves like gutta-percha.

Large quantities of it are imported from Mexico, under the name chicle, into the United States and used in the manufacture of "chewing gum."

It is used chiefly in England as a substitute for gutta-percha and

caoutchouc, and is also used as an addition to these. Towards chloric of sulphur and metallic sulphides it acts like caoutchouc and guttapercha.

- 5. NATURAL VARNISHES.—This term is applied to a class of natural products which are resinous exudations, capable of direct use as vanishes or lacquers. The most important are:
- (1) Burmese lacquer, a thick, grayish terebinthinous liquid, collecte form the Melanorrhæa usitatissima of Burmah. It dissolves in alcoho turpentine oil, and benzene, assuming greater fluidity. Locally, it used in enormous quantities in lacquering furniture, temples, idols, an varnishing vessels for holding liquids.
- (2) Cingalese and Indian lacquer, a black varnish obtained in Cerlon and India from Semicarpus anarcardium, and in Madras, Bomba; and Bengal, from Holigarua longifolia. It forms an excellent varnish adhering strongly to wood and metal.
- (3) Japanese and Chinese lacquer is derived from several species and Chinese lacquer is derived from several species and Chinese fruits form the Japan wax of commerce. (See p. 59.) The lacquer exudes as a milky juice from the trunk of the tree. On exposure to sunlight or when warmed, it loses its moisture and becomes a brown oily liquid to which oils, pigments, etc., are added to form the finishe lacquer. It is most extensively used in Japanese and Chinese lacque work.

# II. Processes of Treatment.

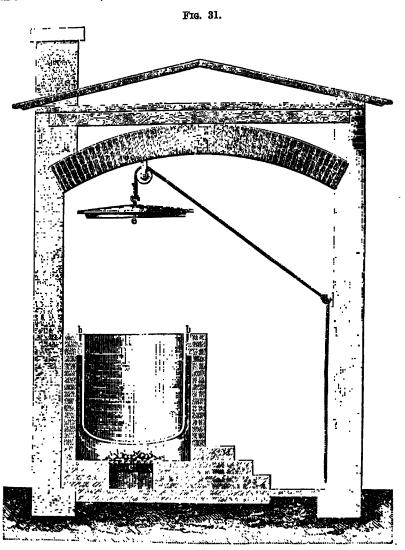
1. MANUFACTURE OF PERFUMES AND SIMILAR PRODUCTS.—In the us of essential oils or mixtures of them, as the basis of agreeable smellir preparations or perfumes, several classes of preparations may be di tinguished: (1) Perfumed waters or alcoholic solutions of mixed esser tial oils; (2) odoriferous extracts or alcoholic extracts from fatty acid charged with odors by "enfleurage" or maceration; and (3) pomadand perfumed soaps. In the manufacture of the first class of prepar tions, the alcohol to be used must be free from fusel-oil and thorough The essential oils may be in part dissolved separately: deodorized. the alcohol or added together to the proper quantity of the solvent a cording to the nature of the materials. Long-continued standing of tl alcoholic solutions is now considered sufficient to effect a thorough ame gamation and development of the desired perfume, and distillation dispensed with. As examples of such perfumes we have the well-know cologne waters and eau de mille fleurs.

The odoriferous extracts are gotten by treating with alcohol the fat oils and fats which have been charged with the perfumes of flowers I the "enfleurage" process. "Glycerine, soft paraffin, and vaseline har latterly been used too in the extraction of the odors. On chilling the alcohol by freezing mixtures or other means to —18° C., the fat separated out and gotten rid of.

Pomades are made from fatty oils, the basis usually being oil almonds, oil of ben, or olive oil. The processes for preparing the

scented fats are those of infusion with warm fatty oils or melted fats at a temperature of about 65° C., and of "enfleurage," or cold perfuming, as already described.

2. Manufacture of Varnishes.—Very much more important, in an industrial sense, is this application of essential oils and resins. Under

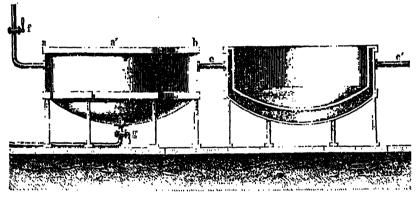


the name varnish is generally understood either a solution of a resin or a rapidly resinifying oil, which, when applied to solid bodies, becomes dry and hard, either by evaporation of the solvent or a drying and oxidation of the same, while the film of resin left behind makes a hard, glossy coating, impervious to air and moisture. Varnishes may be of three classes, according to the character of the solvent used for resin: (1)

Linseed-oil varnishes, in which boiled linseed-oil is used; (2) spirit vanishes, in which alcohol or petroleum spirit is used; (3) turpentine-overnishes.

Linseed-oil Varnishes.—Linseed oil itself, as a drying oil (see p. 54 is capable of forming a varnish without the addition of a resin. F the preparation of varnish, the oil must first be boiled. When heat to 130° C. it begins to boil, but the heat is continued until it shows abo 260° C. (500° F.), which temperature should not be much exceede It absorbs oxygen in this process and becomes thick and glutinous. To absorption of oxygen and the thickeing of the oil are much accelerate by the use of driers like litharge, manganese dioxide, lead acetate, manganese borate, etc. These substances act as "contact substances," morphosphy because of their tendency to form superoxides which the bring about the rapid oxidation of the oil. (See p. 81.) Boilin linseed oil over free fire, as it is generally carried on, is illustrated Fig. 31. Care should be taken that the kettle is not filled so full as





allow it to boil over when strongly heated. The lid e, ordinarily raise can be lowered upon it if the escaping decomposition products catch fit

In Fig. 32 is shown a pair of kettles arranged for boiling the linse oil by steam. Pressures of four and a half to five atmospheres are use for the steam in this case, and a temperature of 132° C. (269.6° F. yielding a perfectly clear, light-colored varnish. When boiled so as have lost one-twelfth of its weight it yields the ordinary boiled oil vanish; if heated until it loses one-sixth of its weight it becomes thick and yields a stiff varnish, which is used as the basis of printers' in (See p. 115.) The specific gravity of boiled linseed oil of good qualivaries from .940 to .950, and on ignition it leaves a mineral residu of from .2 to .4 per cent. Experiment has taught that oxidation preceds the more rapidly when it is pushed rapidly; or, in other word in order to change linseed oil into varnish by atmospheric exposure, must be brought to boiling as rapidly as possible. What takes pla in this case is not an evaporation simply, but a decomposition of the linolein (glyceride of linoleic acid) takes place, whereby glycerine sep

rates, and a portion of the linoleic acid changes into linoleic anhydride,  $C_{32}H_{54}O_{31}$ , an elastic and caoutchouc-like mass (see p. 122), which then dissolves in the undecomposed linseed oil and gives the oil its valuable varnish-forming and drying character. Another part of the linoleic acid, liberated by the boiling, absorbs oxygen and changes into oxylinoleic acid,  $C_{10}H_{20}O_5$ , which at first is of turpentine-like character, while all undecomposed glyceride of linoleic acid dries up to elastic linoxyn,  $C_{32}H_{54}O_{11}$ . A good varnish, therefore, is made up of three factors: (1) Linoleic anhydride, (2) oxylinoleic acid, and (3) linoxyn.

These views of Mulder as to the changes which occur in the boiling of linseed oil are controverted by Bauer and Hazura,\* who consider that the liquid fatty acids of linseed oil consist of eighty per cent. of linolenic and isolinolenic acids ( $C_{18}H_{30}O_2$ ), together with nearly twenty per cent. of linoleic acid ( $C_{18}H_{32}O_2$ ), and small quantities of oleic acid ( $C_{18}H_{34}O_2$ ). They consider Mulder's oxylinoleic acid to have been a mixture, and state that the more linolenic acid an oil contains, the more quickly it dries.

The pure linseed-oil varnish so prepared may then serve for the preparation of what are termed lacquers or solutions of resins in linseed-oil varnish, thinned out ordinarily with turpentine oil or benzine. Of the resins, amber, copal, animé, dammar, and asphalt are used for these lacquers. In order to prepare these varnishes, the resins, amber, copal, etc., are fused in a kettle placed over a coal-fire in such a way that it sinks into the fire-chamber but a slight distance, and the flame can touch the bottom of the kettle only. After the resin has fused, the proper amount of boiling linseed-oil varnish is added, care being taken that the mixture does not fill the kettle to more than two-thirds at the most, and the contents then boiled for ten minutes. When the kettle has cooled down to about 140° C., the necessary amount of turpentine oil is added.

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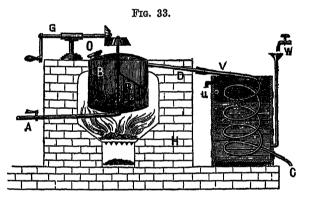
In the case of the two resins, amber and copal, something more than a fusion is essential. They are submitted to a dry distillation, and only after they have given off from ten to twenty per cent. of their weight in oily distillation products does the residue become perfectly soluble. A form of still in which this distillation of resins is carried out is shown in Fig. 33. The copper still B, which is heated in this case over the direct fire, is provided with mechanical agitation, R, and a tube, A, for drawing off the melted residue. This tube is covered where it projects through the fire by fire-brick to protect it from the flame. The distillation products escape through D and are condensed by the worm K. The dry distillation of copal proceeds best at a temperature of 340° to 360° C., while that of amber requires 380° to 400° C. If heated higher than these temperatures the resins become dark. As the melting-point of lead is 334° C., a lead bath is recommended for the copal distillation.

These lacquers are the hardest and most durable of varnishes, but they dry more slowly than simple linseed-oil varnish.

<sup>\*</sup> Zeit. für Angew. Chem., 1888, pp. 455-458.

Spirit varnishes are solutions of resins, such as sandarac, mastidammar, gum-lac, and shellac, in alcohol, although this is sometim replaced by other solvents, such as methyl alcohol, acetone, and petr leum spirit. The spirit varnishes dry rapidly, leaving a brilliant suface, but are more apt to crack and peel off than turpentine varnishe Turpentine is often added to these varnishes to diminish this brittlenes Among the most important varnishes of this class are shellac varnish, which the finest grade is prepared from bleached shellac dissolved alcohol, and copal varnish. In the preparation of this latter, the cop must be first fused, or rather submitted to dry distillation in the mann already described. (See p. 114.) The fused copal residue is afterwar powdered, mixed with sand and covered with strong alcohol, heated boiling for some time and then filtered. The addition of elemi res imparts a toughness to the copal varnish.

Colored spirit varnishes are made by the addition of alcoholic extrac of annatto, dragon's blood, gamboge, turmeric, cochineal, or even sol tions of the different coal-tar colors.



Turpentine-oil Varnishes.—These are prepared in the same way the spirit varnishes. They dry more slowly, but are more flexible at durable. The most important are copal varnish and dammar varnis Turpentine and linseed oil are frequently used jointly in the prepar tion of varnishes, so as to obtain the best results. Thus, in the man facture of copal and amber varnishes, described before (see p. 114), the relative amounts of materials are: Ten parts of copal or amber (or the residue from the distillation of amber oil), twenty to thirty parts a linseed-oil varnish, and twenty-five to thirty parts of oil of turpenting

3. Manufacture of Printer's Ink.—Printer's ink, of whatev grade, whether for newspaper print, for book, lithographic, or coppe plate printing, is a very stiff, rapidly-drying linseed-oil varnish, which has been added lamp-black or charcoal in the finest state of dix sion. For its preparation, linseed, poppy, or nut oil is heated in copp vessels, over a free fire to a temperature beyond the boiling-point, that inflammable vapors are given off. These are frequently ignite or, as is now preferred, they may be allowed to escape into a draugle chimney. The heating is continued until the oil becomes quite thic

and a film forms on the surface, which causes it to swell up with escaping bubbles of vapor. A sample taken out and tested between the fingers should draw out in long filaments. In this condition, with the addition of about sixteen per cent. of lamp-black, the varnish will dry very easily and rapidly. If the varnish has not been boiled long enough, the printed characters will run together and oil will be absorbed in the paper fibre, so that the printed letters will show a yellowish border.

For the ink to be used in book-printing, an addition of soap is absolutely necessary; it allows the inked type to be withdrawn from the moist paper clear and sharp without any adhering or smearing. The finer the printed work required the stiffer and more thoroughly boiled the varnish must be, so that for copperplate and lithographic inks a much stiffer ink is needed than that which is used for newspaper or even book printing. The expensive linseed oil is frequently replaced by hemp-seed, poppy, or nut oil. In order to obviate the necessity of boiling the oil down so thick, rosin is sometimes added to the varnish. Thus, to one hundred and twenty parts of linseed oil forty to fifty parts of rosin are added and twelve to fourteen parts of soap. Rosin oil is also used in place of a part of the linseed oil; indeed, cheap printing ink can be made composed of rosin oil, rosin soap, and lamp-black alone, without the addition of linseed oil at all.

Colored printing inks are obtained by adding to the boiled-oil varnish vermilion, Prussian blue, indigo, and other colors.

4. MANUFACTURE OF OIL-CLOTH, LINOLEUM, ETC .-- In the manufacture of oil-cloths, the basis is a coarse canvas, of jute or cotton stuff usually, which is coated with repeated layers of linseed oil, which has been previously boiled sufficiently with litharge, and to which the coloring matter has been added, or, in other words, a linseed-oil paint. Before putting on the coatings of paint, the canvas is primed with a coating of size. The object of this is not only to give a body to the cloth, but also to protect the fibre from the injurious action of the acid products generated during the oxidation of the linseed oil which is subsequently applied. Cloth which is covered with paint without a protective coating of size soon becomes rotten and brittle. Both sides of the canvas are painted in this way. After thorough drying of this layer a second coat is applied to both sides. This suffices for the back of the oil-cloth. The painting of the face side is continued until it is sufficiently built up for the printing of the pattern. Most of the printing is hand-printing done by blocks, the number of which correspond to the number of colors to be used.

Linoleum is a name often given to a form of oil-cloth in which powdered cork and pigment are incorporated with a thoroughly oxidized linseed oil, which has been brought to the condition of a relatively dry sponge. A pattern may then be printed on and a transparent varnish to cover all.

The oxidized oil used in linoleum manufacture has sometimes both rosin and kauri gum added to it to give it toughness. The proportions for ordinary linoleum are: Oxidized oil, eight and one-half hundredweight; rosin, one hundredweight; kauri gum, one-half hundredweight A variety of linoleum containing wood fibre instead of ground cork h of late years been introduced as a substitute for wall-papering und the name of "lincrusta."

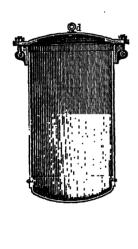
5. Processes of Treatment of Caoutchoug and Gutta-percha. The crude rubber as brought into commerce is quite impure from acc dental causes, and, in many cases, from intentional adulteration. therefore, must undergo a thorough mechanical cleaning before bein submitted to any chemical treatment. It is first boiled with water ( which a little slaked lime is advantageously added) until thorough softened, then cut into slices and passed repeatedly between groove rollers, known as washing rollers, while a stream of cold water flow over it. This crushes and carries away any solid impurities as well those which are soluble. Under this treatment Para rubber loses fro twelve to fifteen per cent. of its weight; the African variety, twent five to thirty-three per cent. After this washing, the rubber is careful and thoroughly dried. Neglect of this frequently causes the war when subsequently vulcanized to appear spongy. The caoutchouc now to be worked over and agglomerated thoroughly, which is do either by passing it repeatedly between rollers heated to 70° or 80° ( or by the aid of the so-called masticating or kneading machine, which consists of a hollow cylinder within which revolves another cylind with a fluted or corrugated surface. The rubber being placed in the annular space between the two cylinders, the inner one is made revolve, whereby the mass is worked over and over and thorough kneaded. The rubber is now to be mixed with the sulphur needed for its vulcanization and with whatever coloring or weighting materia are to be used. This mixing is effected by the aid of horizontal rolle heated internally with steam, and so geared as to move in contrain directions at unequal speed. This mixed rubber so obtained can readi be softened by heat, and can now be shaped, moulded, or rolled in any desired shape, and then submitted to the heat necessary for vi canization.

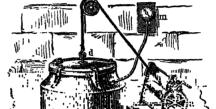
The vulcanization of rubber consists in effecting a combination the caoutchouc with sulphur or sulphides whereby the behavior of the caoutchouc towards heat and towards solvents is changed. Its value for technical purposes is greatly increased by this change.

Two methods of vulcanization are to be noted: (1) the vulcanizin by mixing with sulphur or metallic sulphides and heating to 125° 140° C.; (2) the cold vulcanization process of Alexander Parkes, co sisting of immersing the rubber articles in a solution of chloride sulphur in carbon disulphide or benzene. The latter process is on used for small articles or those consisting of thin layers of caoutchou as the action of the chloride of sulphur, even in the two and one-haper cent. solution usually employed, is very rapid, while at the sar time it is superficial, so that it is difficult to control the action properl In vulcanizing by the first process, that of "burning," as it is terme the crude caoutchour is mixed with varying amounts of sulphur: f

soft rubber goods with about ten per cent., for hard rubber or vulcanite with thirty to thirty-five per cent., of sulphur. Instead of sulphur, metallic sulphides are used, such as alkaline sulphides, sulphide of lead, and sulphide of antimony. For red rubber goods the latter is always used. For soft rubber articles the proper temperature for vulcanization lies between 120° and 136° C.; for hard rubber, from 140° to 142° C. In vulcanizing, only a part of the sulphur is chemically combined, a part remaining mechanically mixed. This can be largely removed by boiling the finished articles in a solution of caustic soda. Both air-baths and steam-baths are in use for heating, the latter at present in the majority of cases. A form of vulcanizing vessel for smaller articles is shown in Fig. 34. The lid can be removed by the mechanism shown at a, and the manometer m shows the pressure existing in the vulcanizer A. This final heating which effects the change

Fig. 34.





in the rubber is frequently called the "curing" of the rubber. Vulcanized rubber goods can be manufactured in the greatest variety of shapes and for a multitude of uses, the rubber being in almost all cases "cured" after the shaping.

In the manufacture of hard-rubber articles, the East Indian, and specially the Java and Borneo, caoutchouc is used, the Para rubber being too expensive, and besides not so well adapted. While in the manufacture of soft rubber the burning or curing was the last process, following the shaping of the articles, in the manufacture of the hard rubber the curing is generally done before the articles are finally shaped. Only in the manufacture of moulded goods is the curing done last. Gutta-percha, balata, and colophony resin are often added to modify the hardness and elasticity, while a large number of mineral substances, such as chalk, gypsum, calcined magnesia, zinc oxide, asphalt, etc., are added chiefly for cheapening purposes. A kind of vulcanite or hard

rubber which contains a very large proportion of vermilion is use under the name of dental rubber, for making artificial gums.

The working over of scrap rubber has in recent years assumed muimportance. Although scraps of raw caoutchouc can easily be knead or rolled together, vulcanized rubber cannot be. The insolubility of tvulcanized rubber in ordinary solvents presents another difficult Although the problem is not yet solved, numerous proposals have bemade. These all involve one of three lines of treatment: (1) mechaical subdivision of the scrap and the adding of the powder so obtain to fresh caoutchouc; (2) heating the vulcanized scrap to fusion aruse of the pitchy mass so obtained as mixing material; (3) partial dsulphurization of the caoutchouc by treatment with acid or alkali und pressure, washing and sheeting of the reclaimed rubber.

Treatment of Gutta-percha.—This is quite similar to that describe under caoutchouc. The crude gutta-percha must be thoroughly washe and freed from dirt and mechanically mixed impurities. It is then cor torn into fine shreds, which are, after washing, heated so as to be them together. It is now kneaded and compacted so as to drive or the air-bubbles.

Gutta-percha is used both in the vulcanized and unvulcanized co dition. The vulcanization is carried out, as in the case of caoutchou by the addition of sulphur and curing. The amount of sulphur vari from six to ten per cent., and the temperature for vulcanization li between 135° and 150° C. The gutta-percha scraps are worked t generally by desulphurizing the vulcanized material by boiling for fit to six hours in a six to eight per cent. solution of caustic soda, washin drying, dissolving in carbon disulphide, benzene, or turpentine, at then distilling off the solvent.

# III. Products.

- 1. Perfumes.—The general character of the several classes of perfumes has already been indicated in the previous section, while the products are so extremely numerous and special in character that are attempt at detail description would be beyond the province of this work
- 2. Varnishes.—We have to note here both the natural varnishes already referred to (see p. 111), and manufactured varnishes. The classification of manufactured varnishes, already given, was: (1) Li seed-oil varnishes, including both plain boiled linseed-oil varnish ar solutions of resins in the boiled oil, or lacquers, as they are often called (2) spirit varnishes, including not only alcoholic solutions of resing but solutions of the latter in benzol, petroleum spirit, wood-naphtha, are other volatile liquids, and (3) turpentine-oil varnishes.

Natural Varnishes.—With regard to the Burmese and Indian la quers, little is known except as to their production as crude materia. The Japanese lacquer has been more fully described, and the method of applying it attentively followed. As the varnish flows from the line incisions in the trees of the Rhus species it is a milky juice, which, or

exposure, quickly darkens and blackens in color. After resting in tubs for some time the juice becomes thick and viscous, the thicker portion settles at the bottom of the vessel, and from it the thinner top stratum is separated by decanting. Both qualities are strained to free them from impurities, and when ready for use they have a rich brown-black color, which, however, in thin layers presents a yellow, transparent aspect. This varnish, when applied to any object, becomes exceedingly hard and unalterable, and with it as a basis all the colored lacquers of Japan are prepared. The black variety of the lacquer is prepared by stirring the crude varnish for a day or two in the open air, by which it becomes a deep brownish-black. Towards the completion of the process, a quantity of highly ferruginous water, or of an infusion of gall-nuts darkened with iron, is mixed with the varnish, and the stirring and exposure are continued till the added water has entirely evaporated, leaving a rich jet-black varnish of proper consistency. In preparing the fine qualities of Japanese lacquer, the material receives numerous coats, and between each coating the surface is carefully ground and smoothed. The final coating is highly polished by rubbing, and the manner in which such lacquered work is finished and ornamented presents endless variations. The durability of Japanese lacquerwork is such that it can be used for vessels to contain hot tea and other food, and it is even unaffected by highly-heated spirituous liquors.

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Linseed-oil Varnishes.—The method of burning linseed or similar drying oil in order to develop its varnish-forming character has been described (see p. 113). The use of metallic oxides and salts as driers has also been referred to. In this connection an additional word may be had. While litharge and lead acetate are commonly used, they must be replaced by manganese or other driers when the boiled oil is to be used as the basis of zinc oxide paint. Lately, manganese borate has been strongly recommended as a drier, and it is asserted that it is capable of giving rapid drying qualities to linseed oil when it is heated a sufficient length of time (from ten to fourteen days) at a temperature of only 40° C. Such a boiled oil would, of course, be lighter in color than if treated at a higher temperature. Liquid driers are also in use at present which have the advantage of acting gradually upon the linseed oil without the aid of heat, so that a boiled oil of very light color is obtainable. These driers contain manganese and lead linoleates and resinates, and concentrated solutions in oil or turpentine are prepared for addition to the oil to be oxidized. Boiled oil is often bleached by sunlight, and always improves by keeping, as impurities gradually settle out, and its drying qualities develop by age.

The most important of the linseed-oil resin varnishes are: Amber varnish, the most durable and resisting oil varnish, but unfortunately of dark color; copal varnish, the finest of all the oil varnishes, nearly as hard and durable as amber varnish, much paler in color, and drying more quickly; and kauri resin and colophony resin for inferior varnishes. The best oil varnishes are made from "fused" copal or amber, with boiled linseed oil, subsequently thinned out with oil of turpentine.

Spirit varnishes are easily obtained perfectly clear; they dry ver rapidly, and leave smooth, lustrous films, which appear at first une ceptionable. But slight vibrations and changes of temperature so develop innumerable small cracks, in consequence of which it loses i lustre, and if the varnish layer was thick it begins to peel off. reason of this is that the film consisted simply of unaltered resin, sprea in a thin layer, and as most of the resins are brittle by nature, slig. shocks or changes of temperature, inducing contraction or expansic of the article varnished, will cause the resin film to break. true of alcoholic varnishes applies, of course, also to all varnishes whe the solvent of the resin takes no part in the formation of the film. The more volatile the solvent the quicker the film is deposited and the easi it cracks. Two methods of obviating this difficulty are in use: first, mix with the brittle resin a soft, balsam-like resin, and, second, to m spirit varnish with one prepared with turpentine oil.

Turpentine varnishes are seldom used exclusively as such because the strong and persistent turpentine odor. When used alone they gir films as perfect as those gotten by the use of spirit varnishes, but tough and drying more slowly than these latter. Usually, however, turper tine oil is used in connection with boiled linseed or other drying oil is varnish manufacture, as in the case given of copal varnish, before discribed. (See p. 114.) The resins used for turpentine-oil varnishes as the varieties of copal, amber, sandarac, dammar, mastic, and coniferous resins.

Japans are simply varnishes that yield, on drying, very hard, bri liant coatings upon paper, wood, or metal, analogous to the natur lacquer of Japan, before described. The effecting of this result is gotte in general by exposing the articles to high temperatures in stoves of hot chambers subsequent to the application of the varnish. This su plementary heating process is called "japanning." It is done with clea transparent varnishes, in black and in colors, but black japan is the most characteristic and common style of work. Black japan varnis contains asphaltum as the basis, and when applied in several layer each of which is separately dried in the stove at a heat rising to 300° ] (149° C.), is susceptible of a high polish. Japanning may be regarde as a process intermediate between ordinary painting and enamellin It is very extensively applied in the finishing of ordinary hardway goods and domestic iron-work, deed-boxes, clock-dials, and papie maché articles. The process is also applied to blocks of slate for makir imitation of black and other marbles for chimney-pieces, etc., and modified form of japanning is employed for prepared enamel, japa or patent leather.

- 3. Printing Inks.—The character of printing inks has been sufciently indicated in the description of their manufacture. (See p. 115
- 4. MISCELLANEOUS PRODUCTS FROM RESINS AND ESSENTIAL OILS.
  (1) Scaling-wax is a valuable product of manufacture from shella Venice turpentine is always added to the shellac to make it more fusib and less brittle, and some mineral coloring matter, which, in the case

the common red variety, is always vermilion. For black sealing-wax the best ivory-black is used, for golden-colored wax, "mosaic gold" (stannic sulphide), for green wax, powdered verdigris. For the commoner varieties, earthy materials, like chalk, magnesia, burnt plaster, barytes, or infusorial earth, are added for the double purpose of making it less fusible and to weight it. Perfumed sealing-waxes are scented with benzoin, Peru and Tolu balsams, and storax. As a substitute for, or adulterant of, shellac in the manufacture of sealing-wax, gum acaroides has recently come into use.

- (2) Rosin Oil.—In recent years great importance has attached to the products of the dry distillation of common colophony resin or "rosin." It yields, on distillation, two valuable products: first, from three to seven per cent. of a light fraction known as rosin spirit, or "pinoline," and, second, from seventy to eighty-five per cent. of rosin oil, a violetblue fluorescing liquid, varying in specific gravity from .98 to 1.1. The pinoline is used as an illuminant and as a substitute for turpentine oil in varnish manufacture. The rosin oil has a large use as a lubricant. especially for machinery and wagon-wheels. It is used in the condition of "rosin grease" (made by stirring rosin oil with the milk of lime), and largely as a substitute for linseed oil in the manufacture of printers' ink. (See p. 115.) Moreover, as it can be deprived of its fluorescence or "bloom" in various ways (exposure to sunlight, treatment with hydrogen peroxide, nitro-benzene, dinitro-naphthalene, etc.), it can be used in adulterating olive, rape, and sperm oils. The best mineral lubricating oils are also adulterated with it at times.
- (3) Oil-cloth and Linoleum.—The general outlines of the manufacture of these products, as given on page 116, allow one to form an idea of the character of them.

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Oil-cloth is a firm but flexible fabric, which by its treatment has been made water-proof and impervious to atmospheric influences. It can be washed and cleansed, and, under ordinary wear, retains for a considerable time its lustre and brilliancy of printed pattern. It is, however, cold and hard, and, unless well seasoned, the pattern is liable to wear off. The covering film will not stand much bending without cracking, and then it rapidly disintegrates.

Linoleum is softer and more elastic to the feet, and, if the composition has been properly made, shows great elasticity and toughness, so that its wearing powers are notably greater than those of oil-cloth. In laying down linoleum, the edges may be cemented to the floor by using a thick solution of shellac in methylated spirit.

- (4) Linseed-oil Caoutchouc.—For the preparation of this substitute for caoutchouc, linseed oil is heated to a high temperature for a considerable time until it becomes dark and has changed into a tough mass. It is stated that when vulcanized by the aid of sulphur chloride it can be used as a substitute or adulterant of genuine caoutchouc.
- 5. INDIA-RUBBER AND GUTTA-PERCHA PRODUCTS.—In noting the properties of crude caoutchouc it was stated that the raw caoutchouc, while elastic at ordinary temperatures, did not show the same character when

chilled, as it became hard, and when heated it lost the elastic featu On the other hand, vulcanized caoutchouc or manufacture rubber shows no change in its elasticity, even within very wide limit of temperature. Freshly-cut surfaces, on being pressed together, w not adhere, as is the case with raw caoutchouc; it swells up only slight in bisulphide of carbon, oil of turpentine, and other solvents, while t raw caoutchouc swells up greatly and even dissolves in part. The vi canized rubber is much more impervious to water than the raw mat rial. As stated before, not all of the sulphur present in the vulcanize rubber is chemically combined. A large excess of uncombined sulph is, however, deleterious to the goods, as it causes them to lose their ele ticity when they are stored for a few years. If such goods are treat with alkaline solutions, the free sulphur can be removed without impai ing the elastic character of the vulcanized caoutchouc. Hard rubbe prepared, as described before, from crude caoutchoue, with a large percentage of sulphur, has a black color and takes a high degree polish. Articles of this material can also be gotten of any desired cold as in the case of the dental rubber previously referred to. Resins, lil shellac, are often added to give elasticity to the hard rubber, the amoun of resin capable of being taken up being considerable, equalling at tim fifty per cent. of the combined weight of the caoutchouc and sulphu Hard rubber becomes strongly electrified by rubbing, and hence is use in various plate electrical machines, while its non-conducting qualitimake it valuable for insulators in various forms of telegraphic app ratus. Hard rubber is unacted upon by strong mineral acids and other chemicals, and hence is used for acid-pumps and connections, for spa ulas, photographic dishes, etc.

Rubber substitute, or so-called "artificial rubber," is made by actir upon linseed, rape, poppy, hemp, and cotton-seed oils with sulphichloride, and removing the hydrogen chloride formed by after-trea ment with milk of lime. The result is a tough rubber-like mass, which however, becomes more or less brittle on keeping.

It is asserted that a better product is obtained by using oxidized of blown 'oils for the treatment with the sulphur chloride. The activated into a rubbin substitute by heating and removal of the free acid.

Gutta-percha, in the pure as well as the vulcanized condition, he been adapted to a multitude of uses. One of the most important uses of gutta-percha is as a material for the matrices or moulds for coin medals, smaller art eastings, etc., and all forms of galvano-plastic wor. The pure gutta-percha serves very well to take imprints, but for ove laying matrices or moulds compositions of gutta-percha and caoutchoumust be used, to unite plasticity when heated with sufficient elasticit to allow of the matrix being removed without injury to the impression. The chief use for gutta-percha, however, is for telegraphic cable instilation (every nautical mile of cable requiring about one-half of a to of gutta-percha), and the chief purchaser and worker in gutta-perch therefore, is the "Telegraph Construction and Maintenance Company,

of London, who buy up the crude gutta-percha through their agents: Singapore. The gutta-percha is covered upon the wires by pressin The partly vulcanized and warm gutta-percha mass is forced out of powerful press along with and around the wire or wires to be covere The gutta-percha must have previously been well kneaded to remove the air thoroughly from it, so that it may pack uniformly.

Gutta-percha is also incorporated with powdered wood and say dust, making a composition which is very hard and can be worked at means of the saw and turning-lathe into a variety of shapes.

# IV. Analytical Tests and Methods.

1. FOR ESSENTIAL OILS.—Essential oils are extremely liable to adu teration, the high price of many of the finer ones lending to this tendency. The usual adulterations are with alcohol, chloroform, oil of turpentine, fixed oils, both vegetable and mineral, and spermaceti, and by mixing the cheaper essential oils with the more expensive. The exadetermination of physical constants, such as specific gravity and optical rotation, becomes, therefore, very important as well as the recognitio of characteristic chemical constituents.

The detection of fatty oils, resins, or spermaceti can often be effecte by simply placing a drop of a suspected oil upon a piece of white pape and exposing it for a short time to heat. If the oil is pure it wi entirely evaporate; but if one of these adulterants be present, a greas or translucent stain will be left on the paper. These substances wi also remain undissolved when the oil is agitated with thrice its volum of rectified spirit.

Alcohol in essential oils may be detected by agitating the oil wit small pieces of dry calcium chloride. These remain unaltered in a pur essential oil, but dissolve in one containing alcohol, and the resultin solution separates, forming a distinct stratum at the bottom of the vesse When only a very little alcohol is present, the pieces merely chang their form and exhibit the action of the solvent on their angles or edge which become more or less obtuse or rounded. If the experiment b performed in a graduated tube and a known measure of the oil en ployed, the diminution in its volume will give that of the alcohol mixe Dragendorff recommends the use of metallic sodium, which does not act on hydrocarbons, and but slightly in the cold on oxygenate essential oils if pure and dry, but in the presence of ten or even five pe cent. of alcohol a small piece of the sodium is dissolved, while a bris evolution of gas takes place. Aniline-red (magenta) is insoluble it essential oils if pure and dry, but in the presence of a small proportio: of alcohol they acquire a pink or red color. This adulteration wit alcohol is said to be very common, as it is a frequent practice of drug gists to add a little of the strongest rectified spirit to their essentia oils to render them transparent, especially in cold weather. Oil of cassiis a notable example of an oil treated in this way.

The adulteration of essential oils with fixed oils is best distinguished

by what is termed "steam distillation." The essential oils all dis over with steam at 100° C., while resinous matters and fixed oils, add as adulterants, will remain in the retort. The adulteration of the fin essential oils with cheaper essential oils is constantly met with. The the expensive oil of cassia is adulterated with oil of cedarwood; oil rose with oil of geranium; and oil of geranium with oil of turpentir Noting the specific gravity carefully where that is characteristic, as noting the odor on evaporating, are methods most generally resorted for the detection of these fraudulent admixtures.

In the case of such oils as contain esters, such as oils of peppermi and rosemary, the percentage of menthyl acetate, bornyl acetate, et can be ascertained by a saponification with half-normal potassium h droxide solution. The free alcohol also present in these oils is the determined by an acetylization with acetic anhydride and anhydro sodium acetate, followed by a saponification test made upon the washe and dried acetylized oil. Exact directions for carrying out these determinations with official essential oils are given in the U. S. Pharm copæia.

The phenolic constituents of certain essential oils like the eugen of oils of cloves and pimenta and the thymol of oil of thyme can also be determined by the use of aqueous solutions of sodium or potassium hydroxide and reading off the loss in the oily layer which ensues a shaking.

The purity of oil of turpentine, as commercially the most importar of the essential oils, is often a question to be determined. The most usual adulterants of oil of turpentine are light petroleum-naphth known as "turpentine substitute," "rosin spirit," and of late a scalled "light camphor oil," gotten as a side-product in the manufactur of safrol. The following tabular statement of Allen\* shows the characters of oil of turpentine, rosin spirit, and petroleum-naphtha undo the influence of different reagents:

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	Turpentine oil.	Rosin spirit.	Petroleum-naphtha.	
1. Optical activity 2. Specific gravity 8. Temperature of distillation. C		Usually none. .856 to .880. Gradual rise.	None. .700 to .740. Gradual rise.	
4. Action in the cold on coal-tar pitch.	Readily dissolves pitch to a deep-brown solu- tion.	Readily dissolves pitch to a deep-brown solu- tion.	Very slight action, lit tle or no color.	
5. Behavior with absolute phenol, 3 of sample to 1 of phenol, at 20° C.	Homogeneous mix- ture.	Homogeneous mix- ture.	No apparent solution.	
6. Behavior on shak- ing 3 parts of cold sample with 1 part castor oil.	Homogeneous mix- ture.	Homogeneous mix- ture.	Liquid separates into two layers of nearly equal volume.	
7. Bromine absorption. 8. Behavior with sulphuric acid.	203 to 236. Almost completely polymerized.	184 to 203. Polymerized.	10 to 20. Very little action.	

It will be seen that the presence of petroleum spirit can be indicate by almost all of these reagents, while that of rosin spirit would hardl

<sup>\*</sup> Allen, Commercial Org. Anal., 2d ed., ii, p. 439.

be shown. H. E. Armstrong\* recommends a process which consists of agitating the suspected turpentine sample first with sulphuric acid and water (2:1), carefully avoiding too high a rise of temperature. This gradually polymerizes the genuine oil of turpentine, changing it to a viscid non-volatile oil. The sample is then distilled with steam, and that which is volatile at this temperature is now treated with 4:1 sulphuric acid and water. The polymerization of the turpentine is usually completed by this treatment, while any petroleum-naphtha present is not affected, and remains as volatile as before. A final steam distillation will give the petroleum-naphtha originally present in the turpentine sample. Rosin spirit is partly polymerized in this treatment, while volatile hydrocarbons remain, but its presence is much harder to indicate certainly than that of petroleum.

Dunwoody has shown that mixtures of turpentine and petroleum are much less soluble in ninety-nine per cent. acetic acid than pure turpentine. While ten cubic centimetres of pure turpentine are soluble in an equal volume of a mixture of ninety-nine parts glacial acetic acid and one part water, it requires forty cubic centimetres of such mixture when the turpentine contains ten per cent. of petroleum, sixty cubic centimetres if twenty per cent. of petroleum be present, and so on in increasing rates.

The Prussian custom regulations prescribe a similar test with aniline oil. Ten cubic centimetres of the sample are shaken up in a stoppered jar with ten cubic centimetres of aniline oil. If pure turpentine is used, a clear solution follows; if petroleum is present, two layers are formed.

The oxidizing effect of fuming nitric acid is also availed of to detect the presence of mineral oil in turpentine, as the latter is entirely oxidized, while the former is not affected. With a pure or nearly pure turpentine the action, however, is so violent as to be dangerous. The presence of rosin spirit in turpentine oil is said to be detected by shaking the suspected sample with an aqueous solution of sulphurous acid. This imparts a bright yellow color to rosin spirit but does not color pure turpentine, benzene or gasolene.

The iodine absorption percentages with Hübl's reagent (see p. 89) for a large number of essential oils have been determined by R. H. Davies,† who finds that the differences in absorption power are very much greater in the case of essential than in that of fixed oils. Some volatile oils do not absorb any appreciable amount of iodine, while others will remove from solution four times their weight, or four hundred per cent. Thus, oil of turpentine shows an absorption equivalent of three hundred and seventy-seven per cent., and wood turpentine two hundred and twelve per cent.

2. For Resins.—The tests for resins or resin acids, when admixed

<sup>\*</sup> Journ. Soc. Chem. Ind., i, p. 480.

<sup>†</sup> Phar. Journ. and Trans., April, 1889, p. 821, and Amer. Journ. of Phar., 1889, p. 301.

with fats or fatty oils, have been referred to under the discussion of the latter. (See p. 91.)

From admixture with the neutral fixed oils resins may be separated by treating the mixture with alcohol of about .85 specific gravity. The alcohol is subsequently separated, and the dissolved resin recovered by evaporating it to dryness. Acid resins, such as common colophony, may be separated from the neutral fats by boiling the substance with a strong solution of sodium bicarbonate or borax. After cooling, the aqueous liquid is separated from the oil and the resin precipitated from its solution in the sodium salt by adding hydrochloric acid.

Resins may be separated from the essential oils and camphors in admixture with which they so frequently occur by distilling in a current of steam.

The resins show some considerable differences when examined by the two methods of bromine absorption and saponification equivalent, before referred to under the fatty oils. (See p. 88.) Mills and Muter\* have determined the bromine absorptions, and E. J. Mills† the proportions of potash neutralized by various resins. The following table gives a summary of their results:

Kind of Resin.	KOH neutralized per cent.	Saponification equivalent.	Bromine absorption.	Hydrobromic acid formed.
Rosin (refined)	18.1 23.0 18.2 22.3 16.1 9.5 15.5 12.4 12.9 16.4 12.9 21.0 5.2 8.8 11.7	308.6 242.7 806.9 256.0 847.6 585.5 861.1 450.8 433.4 840.6 433.4 1068.1 1097.9 478.6	112.7 5.2 4.6 38.9 53.5 60.2 71.6 89.9 84.5 96.4 108.2 108.5 117.9 122.2 124.3	Some. Some. Some. Much. Much. Much. Very much. Very much. Very much.

For the detection of rosin as an adulterant of shellac the Storch reaction with acetic anhydride may be used. A more delicate reaction, recommended by Parry, is to dissolve the sample in alcohol, pour the solution into water and collect on a filter the impalpable powder, which is then dried and rubbed up with petroleum ether. This solution after filtration is shaken up with water containing a trace of copper acetate. In the presence of rosin the petroleum ether is colored emerald green. Pure shellac gives no color.

The constantly-widening use of rosin oil makes the tests for its presence of considerable importance. Rosin oil gives a characteristic violet color with anhydrous stannic chloride or bromide. If it is mixed

<sup>\*</sup> Journ. Soc. Chem. Ind., iv, p. 97.

with fatty oils, A. H. Allen points out that the test may still be successfully applied by distilling the mixture and applying the test to the first fraction which passes over.

Demski and Morawski\* recommend the use of acetone for the detection and rough determination of rosin oil in mineral oils. According to these chemists, rosin oils are miscible with acetone in all proportions. while mineral oils require several times their volume of acetone to effect solution. The test is applied by agitating fifty cubic centimetres of the sample with twenty-five cubic centimetres of acetone. If, on allowing the mixture to stand, it separates into two layers, ten cubic centimetres of the upper or acetonic layer should be removed with a pipette and evaporated, and the residual oil weighed. In the case of pure American or Galician lubricating oil the residue will weigh about two grammes. but only half this quantity will be obtained from Wallachian or Caucasian oil. It is stated that mixtures of rosin oil with the lubricating oils from American and Galician petroleum are permanently soluble in half their volume of acetone, if the proportion of rosin oil exceeds thirty-five per cent, of the mixed oil, but that complete solution is not effected in the case of Wallachian and Caucasian oils unless the rosin oil constitutes at least fifty per cent. of the mixture. Ragosine cylinder oil requires an addition of rosin oil equal to fifty-three per cent. of the mixture to become soluble in half its volume of acetone.

- 3. For Varnishes.—The most important constituent which enters into the manufacture of varnishes is undoubtedly the linseed or other drying oil. Linseed oil (see p. 54) is liable to be adulterated with other vegetable oils, with fish oils, with mineral and rosin oils, and with rosin itself. As mineral and foreign seed oils are lighter in specific gravity than linseed oil, while rosin and rosin oil are much heavier, by the judicious use of a suitable mixture of mineral and rosin oils extensive adulteration can be effected without alteration of the density. The analysis of a linseed oil supposed to be adulterated would be made according to the scheme given before (see p. 92) for the analysis of a fatty oil containing foreign admixtures. A. H. Allen gives also a rather elaborate method, which he states is better adapted for a boiled linseed oil, for the details of which the reader is referred to Allen's "Commercial Organic Analysis," 3d ed., vol. ii, Part ii, p. 155.
- 4. For Caoutchouc and Gutta-percha.—The adulterations of caoutchouc are both mineral, or inorganic, and organic in character. A careful incineration of a given specimen in a porcelain crucible will leave any mineral admixture, as ash. Oxide of zinc, gypsum, and such admixtures are thus recognized. As many samples of vulcanized rubber now contain cheapening agents of an organic nature, such as oils and rubber substitutes added for the purpose of cheapening the product, some more complete method of analysis is needed to enable one to distinguish them. Weber has proposed a method of fractional solution by the aid of different solvents that has been largely used. The sample is first extracted with acetone, which dissolves out fatty oils,

mineral oils, resin oils, resins, and free sulphur. The residue from this extraction may then be extracted with pyridine to take out pitch and bituminous bodies. This is followed by a treatment with alcoholic potash which will saponify and extract oxidized or blown oils and the chlorosulphide compounds of the same. The residue from this treatment will contain the true rubber and the sulphur of vulcanization. together with inorganic filling materials. The rubber of this residue is then to be determined either by extraction with α-nitronaphthalene, or by converting it into a nitrosite by the action of nitrogen peroxide gas on the residue suspended in dry chloroform or benzene.

The total sulphur having been determined on a separate sample by the aid of strong nitric acid or sodium peroxide, and the free sulphur having been obtained from the acetone extract, the sulphur of vulcanization is obtained by difference after allowing for any sulphur found in the mineral residue.

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#### STATISTICS.

No attempt will be made to take up the essential oils in detail. The statistics of the entire class will be given, and only a few of the more important substances will be specially mentioned.

Essential Oils.—The export of essential oils (bergamot, lemon, etc. from Sicily and Calabria in recent years has been:

	Kilos.	Value in lire.
1903	864,770	11,964,839
1904	1,006,103	14,758,590
1905	868,244	13,759,760
1906	948,328	18,556,053
1907	1,056,898	24,173,030

The Bulgarian rose oil exportations for recent years have been:

1906.	1907.
5700 kilos.	<b>3</b> 900 kilos.
Value 4,590,938 francs	3,432,327 francs

Peppermint oil is exported from Japan in the forms of menthe crystals and dementholized oil. The statements of production, therefore, include both of these sources.

The exports of these two in recent years have been as follows:

	1904.	1905.	1906.
Menthol crystals	86,489 kilos.	100,240 kilos.	57,329 kilos.
Value\$	968,579	\$708,290	\$459,287
Peppermint oil	104,861 kilos.	104,344 kilos.	72,682 kilos.
Value \$	40G 347	\$436 537	\$320 872

The American production of peppermint oil for 1907 was estimate by Schimmel & Co. at 230,000 pounds, of which New York furnishe 28,000 pounds and Michigan and Indiana 205,000 pounds.

The exports of cinnamon chips, for the extraction of oil of cinn mon, from Ceylon in recent years have been:

1901	1,516,083 p	ounds.	1904	2,368,351	pounds.
1902	1,763,679	"	1905	2,325,514	"
1903	2,253,269	"	1906	2,531,614	"

The total exports of chips average about one-half by weight of the total exports of Ceylon cinnamon bark. The world's consumption abark and chips together during the last few years has been in rour numbers 3,500,000 pounds a year.

The exports of citronella oil from Ceylon (Colombo and Galle) habeen as follows in recent years:

1904 1905		1906 1907	1,242,110 pounds.
	_,,		Report, April, 1908.)

The production of spirit of turpentine in the United States amoun at present to about 25,000,000 gallons, of a value of about \$8,500,000.

The exportations of turpentine spirit from the United States during the five years stated were:

```
    1908.
    1904.
    1905.
    1906.
    1907.

    Gallons .......
    16,378,787
    17,202,808
    15,894,813
    15,981,253
    15,854,676

    Valued at ..
    $8,014,322
    $9,446,155
    $8,902,101
    $10,077,268
    $10,241,883
```

Camphor.—The production of camphor and camphor oil in greater Japan (including Formosa) during the last few years amounted to:

```
1905. 1906. 1907. Camphor ...... 5,469,733 lbs. 5,581,200 lbs. 5,388,918 lbs. Camphor oil .. 4,556,666 " 4,644,400 " 6,710,390 "
```

The export of camphor in 1907 was 4,121,566 pounds, valued at 5,026,858 yen. The production of camphor in China is given as follows:

```
1906. 1907. 1,500,000 lbs. 2,250,000 lbs. (to end of August)
```

The world's consumption of camphor is estimated at 10,000,000 pounds yearly, of which seventy per cent. is used in the manufacture of celluloid, two per cent. in the manufacture of gun cotton, fifteen per cent. for disinfection, and thirteen per cent. for medicinal uses.—

Zeit. für Angew. Chemie, 1908, p. 1201.

Resins.—The exportations of rosin (colophony resin) from the United States for the last five years have been as follows:

```
1903. 1904. 1905. 1906. 1907.

Barrels ...... 2,396,498 2,585,108 2,310,275 2,438,556 2,560,966

Valued at .. $4,817,205 $6,621,870 $7,069,084 $9,899,080 $11,327,091
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The exports of button lac and shellac from British India during recent years have been as follows:

	March 31, 1906.	To March, 1907.	To March, 1908.
Pounds	29,053,920	27,153,392	35,580,832.
Value	\$10,297,000	\$11,152,286	\$12,707,440

The importation of the more important gums and resins into the United States during the past five years has been:

	1903.	1904.	1905.	1906.	1907.
Crude camphor (lbs.)	2,472,440	2,819,673	1,904,002	1,668,744	3,669,880
Value	\$764,400	\$874,695	\$638,744	\$608,440	\$1,932,073
Chicle (lbs.)	4,282,247	5,084,580	5,060,166	5,828,641	6,768,470
Value	\$954,389	\$1,308,540	\$1,357,458	\$1,657,587	\$2,239,441
Copal, kauri, and dammar					
(lbs.)2	7,653,928	20,565,507	25,687,762	23,063,509	28,021,930
Value\$	2,938,754	\$2,127,228	\$2,493,438	\$2,353,888	\$3,126,737
Shellac (lbs.)1	1,590,725	10,933,413	10,700,817	15,937,763	18,418,135
Value\$	2,713,687	\$3,505,229	\$3,743,180	\$5,200,449	\$6,346,221

An estimate of the annual production and consumption of caoutchouc throughout the world in recent years is as follows:

		Production.		Consum	ption.
1901-02	!	53,887	tons.	54,110	tons.
1902-03	(	55,603	"	55,276	**
1903-04	(	61,759	"	59,266	66
1904-05	(	68,879	46	65,083	**
1905-06		67,899	66	62,574	**
1906-07		74.023	66	68,173	ÇE

About half of the product of 1907 was Para rubber.

Gutta-percha.—The entire world's production of gutta-percha in 1890 was estimated at 4,500,000 kilos. This amount has decreased notably since 1890, amounting in 1896 to only 2,600,000 kilos., and in 1901 to 2,400,000 kilos.

The United States importations of crude caoutchouc and guttapercha with related substances of the last few years have been:

	1905.	1906.	1907.
Gutta-percha (lbs.)	665,217	500,770	546,890
Value	\$210,188	\$188,161	\$201,339
Gutta-joolatong (lbs.)	19,104,911	21,390,116	28,437,660
Value		\$733,074	\$1,085,098
India rubber (lbs.)	67,234,256	57,844,345	76,963,838
Value	349,878,366	\$45,114,450	\$58,919,981
India rubber scrap (lbs.)	15,575,214	24,756,486	29,335,193
Value	\$953,439	\$1,721,678	\$2,608,987

The exportation of balata from South American countries in recent years has been:

	1904.	1905.	1906.	1907.
From British Guiana (lbs.)	800,133	774,665	728,231	834,728
Value	£66,996	£54,837	£53,011	£64,094
From Venezuela (lbs.)			1,232,148	1,455,973
Value			£176,039	£224,414
From Dutch Guiana (lbs.)	259,000	244,000	270,000	
Value	£37,904	£34,630	£44,990	

#### CHAPTER IV.

#### THE CANE-SUGAR INDUSTRY.

## I. Raw Materials.

ALTHOUGH sucrose, or cane-sugar, is present in a great many plants, it is usually accompanied by relatively large quantities of other carbohydrates, such as glucose, starch, etc., so that its extraction on a commercial scale is practically impossible. In order to extract the cane-sugar advantageously, glucose, invert sugar, and other dissolved solids must not be present in amount relatively large as compared with the sucrose. If this ratio of sucrose to total dissolved solids, called the "coefficient of purity," falls below a certain percentage (usually put at sixty-five), the plant-juice cannot be economically worked for the extraction of crystallized cane-sugar. At the present time the sucrose is extracted from four different sources, and on what may be termed a commercial scale from two only.

I. The Sugar-cane.—The sugar-cane belongs to the family of grasses, growing, however, to an exceptionally large size. The plant is known as Saccharum officinarum, and the best known varieties are called by such names as Bourbon cane, Otaheite purple cane, ribbon cane, crystalline cane, and Java cane. It has a wide range, succeeding in almost all tropical and sub-tropical countries, and requires a warm, moist climate, developing most luxuriantly on islands and sea-coasts in the tropics. It is the richest in sugar of all the plants cultivated for this purpose. Under ordinary favorable conditions it yields about ninety per cent. of juice, which contains eighteen to twenty per cent. of crystallizable cane-sugar. The following analyses of sugar-canes from several sources illustrate its composition:

	Martinique. (Peligot.)	Guadeloupe. (Dupuy.)	Mauritius. (Icery.)	Martinique. (Popp.)	MiddleEgypt. (Popp.)	Upper Egypt. (Popp.)	
Water Sucrose Glucose . Cellulose . Salts	72.1 18.0 	72.0 17.8  9.8 0.4	69.0 20.0 10.0 0.7 to 1.2	72.22 17.80 0.28 9.30 0.40	72.15 16.00 2.30 9.20 0.85	72.13 18.10 0.25 9.10 0.42	
	100.00	100.00	99.7 to 100.2	100.00	100.00	100.00	

The most successful cultivation of the sugar-cane is at present carried on in Cuba and other West Indian islands, and on the irrigated, fertile, volcanic soils of Hawaii.

2. Sugar-beet is a source of sucrose that, whi first mentioned as long ago as 1747, when Marggraf called the attentic of the Berlin Academy of Sciences to its importance as a sugar-yieldir material, has only in the last few decades advanced to great important and taken position as a successful rival of the sugar-cane in the matte of production. It has been greatly improved by careful selection ar cultivation, and its richness in sugar notably increased. Marggraf cou only extract 6.2 per cent. of sugar from the white and 4.5 per cen from the red beet; it has now been brought to an average of eleven pe cent., and in exceptional cases has been found to contain eighteen pe cent. Some six varieties are now cultivated in Germany, where tl beet-sugar industry has reached its highest development: the whi Silesian, the Quedlinburg, the Siberian, the French, the Imperial, ar the Electoral. (The beet is relatively much more complex in its cher ical composition than the sugar-cane, and the expressed juice contain a number of organic impurities not present in the juice of the can notably of the class of nitrogenous or albuminoid substances. On the other hand, glucose, or invert sugar, which is frequently present in tl cane, is practically absent in the juice of fresh beets.) The details composition of the sugar-beet is seen from the accompanying scheme Scheibler.\* At the same time the three accompanying analyses by 1 Hofmann give the composition of three types of beets: those poor i sugar, those of medium richness, and those containing the largest pe centage.

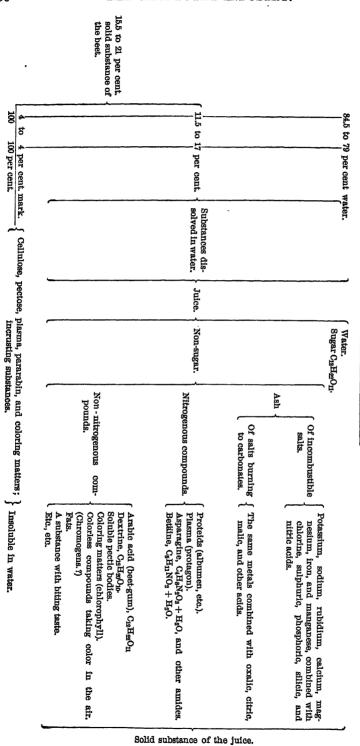
	First type.	Second type.	Third type
Water Sugar Nitrogenous compounds Non-nitrogenous { soluble compounds { insoluble (cellulose)	89.20 4.00 1.00 4.18 1.01 0.66	83.20 9.42 1.64 8.84 1.50 0.90	75.20 15.00 2.20 4.28 2.07 1.30
	100.00	100.00	100.00

3. Sorghum Plant.—The sorghum plant (Sorghum saccharatue and other species) has been known and valued in China for ages, an small quantities have been cultivated in the United States for the sal of the syrup for a number of years past. It is only of recent year however, that attention has been drawn to it as a source of crystallize sugar, chiefly by the experiments of the United States Bureau of Agr culture, and its systematic cultivation has been attempted in sever parts of the United States. The composition and saccharine strengt of the juice seem to be quite variable, and dependent upon condition of cultivation to a much greater extent than is the case with either the sugar-beet or the sugar-cane. Thus, in 1883 the mean per cent.

<sup>\*</sup> Bericht über Entwick Chem. Ind., von Hofmann, 1877, 3te Heft, p. 187.

# GENERAL VIEW OF THE COMPOSITION OF THE SUGAR-BEET.

4



sucrose in the sorghum juice, analyzed by the chemists of the depar ment, was 8.65, in 1884 the mean was 14.70 per cent., in 1885 it was 9.23, and in 1886 it was 8.60 per cent. The sorghum plant grows easi over a very wide range of climate, and if its cultivation can be esta lished definitely upon correct principles, it may prove to be a most valable addition to the world's sugar-producing materials.

4. The Sugar-maple.—The sap of Acer saccharinum and othe species of the genus Acer is a source of sugar and syrup more esteeme for confectionery and table use than because of its commercial importance. The sugar is never refined, and only comes into use as a ray small-grained sugar of peculiar and characteristic flavor; the syrup a thin, sweet syrup of the same characteristic maple flavor, differing considerably, too, in its composition from both cane- and beet-sugaryrups. The freshly-collected sap contains from two to four per cent of sucrose, with traces of glucose.

We may now compare the chemical composition of the freshly-expressed juice from the three sources of sugar manufacture above discribed, and note those differences which are of importance in determining the successful extraction and crystallization of the cane-sugar

The composition of the fresh juice of the sugar-cane is illustrated if the following table. The first four analyses are by the United State Bureau of Agriculture and were made in connection with its experimental work, and the last six from experimental cultivation of certain varieties of cane in Cuba on the Soledad estate of Mr. E. Atkins.

	LOUISIANA,				CUBA.					
	1884.	1885.	1886.	1887.	Crystalline cane.		Red ribbon cane.		Black Java cane.	
Specific gravity . Total solids Sucrose Glucose	1.068 16.54 13.05 0.67	15.80 12.11 1.02	1.066 16.20 18.50 0.61	1.066 16.87 13.69 0.77	11.6° B. 20.9 19.2 0.66 Non-	12.5° B. 22.6 20.5 0.20 Non-	11 2° B. 20.2 18.5 0.14 Non-	12.1° B. 21.9 20.0 0.31 Non-	12.2° B. 22.0 21.3 Trace. Non-	11.8° 21.4 20.6 0.08 Non
Albuminoids Coefficient of	0.19	0.16	0.167		sugar. 1.04	sugar. 1.90	sugar. 1.56	sugar. 1.69	sugar. 0.70	suga 0.71 96.3
Albuminoids Coefficient of purity	78.97	76.64	83.33	83,48	91.8	90.7	91.5	91.3	96.8	

It will be seen that under favorable conditions the sucrose percentagin cane-juice may rise to over 20 per cent.

'n

The average composition of the fresh beet juice is shown in the following analyses, the method of obtaining the juice being also indicate The first four are from "Stammer's Lehrbuch," and represent each of the average of a German beet-sugar factory for the season; the fifth from beets cultivated at Washington, D. C., by the Bureau of Agriculture; the sixth the average of a week's work at Alvarado, Californi in 1888, and the last from a beet grown at Grand Island, Nebraska, ar analyzed at the State Agricultural Experiment Station.

	German. By press- ure.	German. By diffu- sion.	German. By cen- trifugat- ing.	German.	Washing- ton. By press- ure.	Alvarado, Cal. By diffu- sion.	Grand Island, Neb.* H. H. Nichol- son.
Total solids (degree Brix.)	16.27 18.02  8.25 80.02	17.20 14.63 2.57 85.14	14.99 11.98  8.01 79.92	18.77 14.64 4.18 77.99	11.78 7.61 0.89 8.78 64.60	17.20 14.80 	28.70 21.41 0.138 2,152 90.8

In 1907, at one factory in California (Los Alamitos) the average for the entire campaign was: sugar, 19.3 per cent., with an average coefficient of purity of 84.8.

The composition of the sorghum juice of different seasons, as cultivated by the United States Department of Agriculture, is shown in the following table:

	1883.	1884.	1885.	1886.	1887.		
				2000,	Fort Scott.	Rio Grande.	
Total solids	13.59 8.65 4.08 0.86 63.65	19.75 14.70 1.27 3.78 74.48	15.07 9.28 8.04 2.80 61.25	17.08 9.59 4.25 8.24 56.15	16.14 9.54 8.40 8.20 59.11	14.02 8.98 8.24 1.80 64.05	

Analyses of fresh maple-sap made at Lunenburg, Vermont, by one of the chemists of the Department of Agriculture, in the spring of 1885, show that it contains an average of 3.50 per cent. of sucrose, traces only of glucose, about .01 per cent. of albuminoids, and has a mean coefficient of purity of 95.

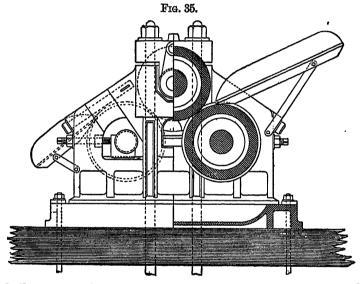
## II. Processes of Treatment.

1. Production of Sugar from the Sugar-cane.—As the cultivation of the sugar-cane is chiefly carried on in the tropical countries. parts of which are dependent upon totally unskilled labor, there is very great diversity in the development which the industry has reached. In some countries the work is still done by hand or with the simplest kind of machinery, with corresponding small yield of inferior products. while, in others, as in Louisiana, Demerara, Cuba and other West Indian islands, there are many sugar plantations equipped with the very latest and best of sugar-making machinery, and producing direct from the juice raw sugars that are almost equal to the refined product. In general, however, the sugars produced on the plantation are not in a sufficiently pure condition for consumption and are termed "raw sugars," having therefore to undergo a process of refining, by which the impurities are eliminated and the sucrose obtained in a pure, well-crystallized We shall note first the method of producing raw sugar, and afterwards the methods of refining the same at present in use.

<sup>\*</sup> Individual beets grown in Nebraska have shown a percentage of 22.08 sucrose, and a coefficient of nurity of ninety-three per cent

The canes must be cut when they have arrived at maturity, ar must be promptly used to prevent the fermentation of the albumino constituents and other non-sugar of the cane, which in turn rapid changes sucrose into invert sugar and lessens the possible yield of cry tallizable sugar. At least this immediate use of the cut cane is necessar in Cuba, Demerara, and distinctly tropical countries, where the juic must be expressed within forty-eight hours after the cutting to prever an excessive inversion taking place. In Louisiana, the experiments the Department of Agriculture have shown\* that sound canes can kept stored under cover for two or three months without appreciab diminution in the sucrose per cent. or loss in the coefficient of purity.

The expression of the juice has been, and in most cases still co tinues to be, effected by the process of crushing the canes between hear rolls, which may vary from the crude stone or iron rolls, driven by wat or horse-power, to the perfected sugar-mills now in use, in which eno

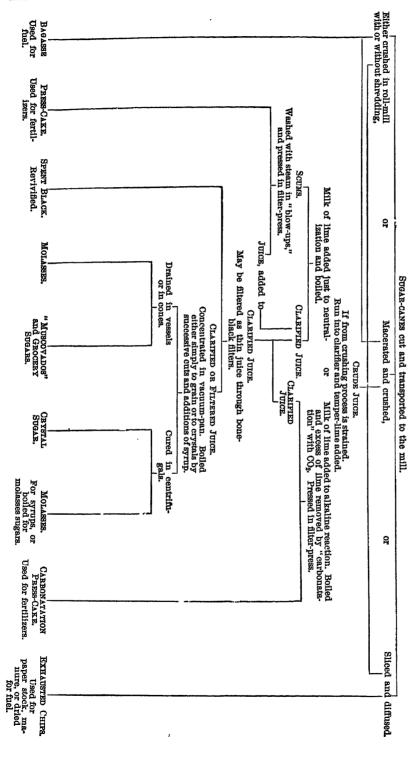


mous, hollow, steam-heated rolls, driven by steam, are used to do the same work. Large, slow-moving rolls have been found in practice yield better results than smaller, rapid-moving rolls. While four, five and even nine-roll mills have been constructed, the mill in general uses a three-roll mill, an example of which is shown in Fig. 35. The campass by the carrier, down the slide, through the rolls, and the "bagasse (exhausted canes) emerging below is carried away for fuel purpose while the juice as expressed collects in a receptacle and is run to the evaporators.

While the analyses of sugar-canes, given on a previous page, sho that the cane contains ninety per cent. of juice, the percentage of e traction of juice by this roller-crushing process on the best-manage Cuban estates does not exceed seventy or seventy-one, and general ranges from sixty to sixty-five, per cent. This imperfect liberation

<sup>\*</sup> Bulletin No. 5, p. 57.

## GENERAL VIEW OF THE PRODUCTION OF SUGAR FROM THE SUGAR-CANE.



the cane juice by the crushing process has led to experiments in other directions. One result has been the frequent introduction of a second or supplementary crushing of the cane in a two-roll mill following the use of the three-roll mill before described. These second rolls are heavier, and the pressure is greater than in the first crushing. The total percentage of juice, and consequently of sugar extracted from the cane, is raised, although the juice from the second and heavier pressure is less rich in sucrose than the first juice, which came from the softer pulp of the cane.

It has also been sought to increase the yield of saccharine juice by submitting the cane to the action of hot water or steam at an intermediate stage between the two crushings. It is stated that a "maceration" process of this kind, known as Duchassing's, has been in quite successful use in Guadeloupe, raising the yield of sugar from 9.40 per cent. on the cane to 11.04 per cent.

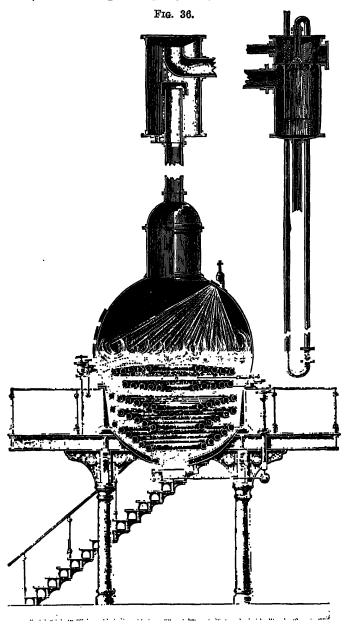
All the processes hitherto described for extracting the juice from the cane have depended for success upon the rupture of the juice-containing cells. "Diffusion," which has been so successful in the extraction of the juice of the sugar-beet, differs from them essentially in dispensing with the breaking up of the cells, and in substituting therefor a displacement by osmosis or diffusion of the saccharine juice by pure water. As a description of this method follows when speaking later of the treatment of the sugar-beet, we will at this stage speak only of the advantages and disadvantages of its application to the sugar-cane work. It has not met at all with general favor from sugar-cane planters. Difficulties were met with in cutting the chips needed for the diffusion-The sugar-cane differs so radically in its structure from the sugar-beet that totally different forms of slicing apparatus had to be used. The cane-chips tended to pack in the cells, and so impeded the circulation of the warm water. When this took place, fermentation and inversion of the sucrose rapidly followed. The cane-chips, after exhaustion, do not make as good a fuel as the bagasse of the cane-mill. The first of these difficulties has been overcome both in the use of diffusion apparatus in Guadeloupe and by the United States Department of Agriculture in its experiments on diffusion, as applied to the sugarcane made at Fort Scott, Kansas, in 1886. The second difficulty has in part been overcome by using hotter diffusion water (at 90° C.), and working more rapidly with a sufficient pressure. But it is more effectually prevented by the use, in the diffusion-cells, of either carbonate of lime, as proposed and patented by Professor M. Swenson, or of dryslacked lime, as proposed by Professor H. W. Wiley, the chemist of the Department of Agriculture. Of these, the latter seems to meet with more general approval of those who have tried diffusion with either the sugar-cane or the sorghum-cane. In answer to the third difficulty, it is remarked that the bagasse burns better largely because of the notable quantity of sugar left in it, and that when the diffusion-chips are dried they will burn fairly. They can also be used to great advantage for paper stock and for manure, as they still contain most of the nitrogenous constitutents of the cane. On the other hand, if successfully carried out, it undoubtedly effects a more complete extraction of the sugar than any other process. At Monrepos, Guadeloupe, with Bouscaren's apparatus, consisting of six diffusors, juice having a density nearly equal to that of the natural juice is obtained, one and a half hours being sufficient for extracting the sugar. The yield of white sugar amounts to twelve and a half to thirteen per cent. of the weight of the cane.\* At Fort Scott, Kansas, the chemists of the Department of Agriculture, in their experiments with diffusion as applied to sugarcanes, succeeded in obtaining a yield the highest ever got from sugar-The mean loss of sugar in the chips at Fort Scott was .38 per cent., and the quantity of sugar present was 9.56. The percentage of extraction was, therefore, ninety-six per cent., or, reckoned on the weight of cane, 86.4 per cent. of a possible ninety, which, if compared with the best figures obtained in mill-crushing shows a decided advantage for diffusion.

The treatment of the expressed juice is next to be noted. This has also undergone considerable improvement in recent years, although on small isolated sugar plantations the primitive and wasteful methods of the "copper-wall," or open-pan, boiling are still in use. The general outline of the treatment of the juice which is followed in the main, if not always in detail, is given in the accompanying scheme.

The juice of the sugar-cane must be properly "defecated," or treated with milk of lime, in order to neutralize the organic acids of the juice, and so prevent their starting a fermentation and consequent inversion of the sucrose when the juice is heated. This has the effect, as soon as the juice is heated, of bringing to the surface a thick scum of lime salts. holding mechanically entangled much of the albuminoids and suspended particles of fibre of the juice. This is known as the "blanket-scum." This is removed by skimming, and the boiling continued, when additional greenish scum forms, which is similarly removed. When the scum ceases to form, the steam is shut off and the sediment allowed to settle, and the clarified juice gradually drawn off. The amount of lime to be added in the case of cane juice is usually .2 to .3 per cent., or about four ounces of quicklime to the gallon of juice, but is always carefully controlled, so that the acids of the juice are not entirely neutralized and a faint acid reaction still remains. Should the lime be in excess, the glucose almost always present in the cane juice is rapidly acted upon and decomposed, yielding dark-colored products. An excess of lime is always corrected before further treatment by the addition of sulphurous, sulphuric, or phosphoric acids. In the older process of open-pan boiling, this defecating and clarifying takes place in the first of five connected kettles or pans, walled in and heated by the same fire, and known technically as the "copper-wall." From this first pan the juice, after the removal of the blanket-scum, goes to the second, in which it receives more heat. After it is thoroughly clarified and both scum and sediment removed, the juice goes to the third and fourth pans succesį

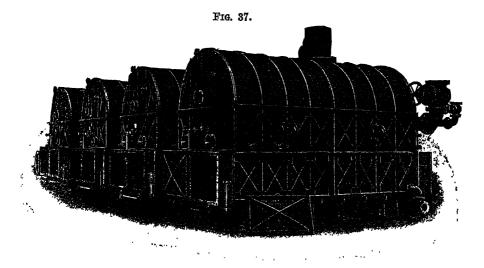
<sup>\*</sup> Spon's Encyclopedia, p. 1881.

sively, in which it is concentrated to 30° B., and then goes to the fifth, or "strike-pan," to be brought to the crystallizing point. When the "masse-cuite," full of separating crystals, has been sufficiently heated,



it is "struck out" into shallow, crystallizing vessels and allowed to cool, and so complete the crystallization. The older open-pan sugars are generally "cured," or freed from syrup, simply by draining in

vessels with perforated bottoms, or, in a limited number of cases, by the process of "claying," or covering the sugar in cones with a batter of clay and water, through which water percolates, slowly displacing the darker syrup. The first method gives the common "muscovado" sugar, a moist, brown sugar, which goes from the West Indies to the United States and Europe for refining; the second method gives a lighter-colored but soft-grained sugar, which similarly must be refined for use. This older and cruder method has given place most generally now to improved methods, whereby the yield is notably increased and grades of raw sugars are produced that are much purer and finer in appearance. The chief improvements consist in the use of vacuum-pans for concentration of the juice and centrifugals for curing the crystallized sugar. At the same time other minor improvements contribute no little to the better results. The juice, unless it has been gotten by diffusion,



is generally run through a strainer into the clarifier. In addition to very careful and exact measuring of the amount of "temper-lime" needed, sulphurous acid or phosphoric acid are added to the juice, followed by lime until the juice is nearly neutralized. On heating the juice becomes bright and thin, most of the gummy impurities being removed by this treatment. It may be passed through bag filters and is then ready for the vacuum pan.

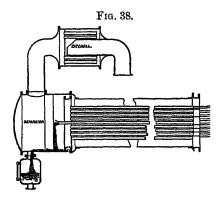
Much raw sugar obtained by the use of sulphuring and vacuum-pan evaporation is well crystallized and nearly white and can be brought into use without refining or bone-black filtration.

The most important improvement in the preparing of a better-grade sugar, however, consists in the use of the vacuum-pan, by means of which the concentration can be effected with the least heating, and hence least discoloring of the sugar-containing juice. The vacuum-pan, invented in 1813 in England by Howard, allows of the concentration,

or "boiling to grain," being effected at temperatures varying from 130 to 170° or 180° F., instead of the 240° or 250° F. reached in the ope pan. They are of varying forms, but consist essentially of a spherical cylindrical, or dome-shaped copper or iron vessel, such as is shown Fig. 36. The contents of this vessel are heated by the steam-coils show in the cut, and the vacuum is maintained by the connection with a injector air-pump, as shown. The vacuum-pan is connected first wi an overflow vessel, or "save-all," to collect saccharine juice throw over, and thence with the exhaust-pump. Through suitable opening in the side of the pan the interior can be illuminated and the operation watched; samples can be withdrawn by the aid of the "proof-stick for examination, and fresh juice can be admitted when the grain is be built up.

In concentrating the raw juice, considerable use is made of what a called "mutiple effect" vacuum-pans, a series of connected pans shown in Fig. 37, in the first of which the thin juice boils under

slightly-reduced pressure and, of course, at a slightly lower temperature than in the air; the vapor from the boiling juice here passes into the steam-drum of the second pan, and readily boils the liquor here, which, though denser, is under a greater vacuum, and similarly the vapor from this liquor boils the most concentrated juice in the third pan, in which, by the aid of the condensing-pump, a very perfect vacuum is maintained. Thus large quanti-



ties of juice are evaporated with great economy of fuel. These trip effects have been much improved in the last few years by the modific tions introduced by Yaryan and Lillie, both of whom adopt the plan sending the sugar juice to be concentrated through the series of co while the steam circulates around these tubes. The action of the Yarys apparatus will be understood from Fig. 38, giving a simplified section through one of the pans and "catch-alls." The heating-tubes, su rounded by steam, are divided into units or sections, consisting of fir tubes coupled at the ends so as to form one passage. Of such section there may be any number. The liquor enters the first tube of the co in a small but continuous stream, and immediately begins to boil vi lently. It is thus formed into a mass of foam, which contains, as rushes along the heated tubes, a constantly-increasing portion of steal The mixture is thus propelled forward at a high velocity, and final escapes into an end chamber known as a "separator," which is providwith baffle-plates.

The "masse-cuite" having been brought to sufficient thickness, t

whole or a part of the contents of the pan are "struck-off." If half the contents of the pan are discharged and fresh syrup then admitted to be concentrated, the crystals obtained at first grow by the deposit from the new portion of syrup. This process of admitting successive portions of fresh syrup after the "grain" has once formed is used in the development of large crystals. It must be used with judgment though, or the new syrup starts a new set of minute crystals, making what is called "false grain." The large yellow Demerara crystals are given the light yellow bloom by admitting sulphuric acid in small amount after the grain is complete and just before the "strike." It destroys the gray-green color of the raw-sugar crystals and gives instead a pale straw color.

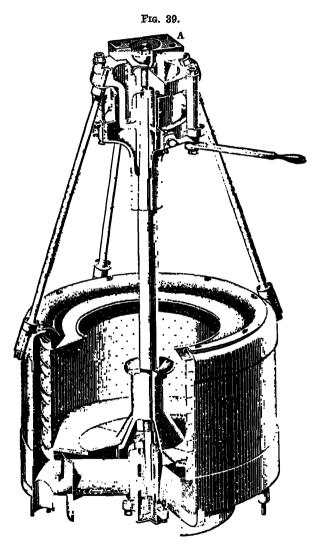
After the "masse-cuite" has left the pan, the crystallization, except in the case of the large crystals, is completed by cooling, and the sugar must then be "cured." This is now generally effected in centrifugals or rotary perforated drums. A form in common use for sugar-work is shown in Fig. 39. Over each centrifugal is a discharge-pipe from the coolers; the brown or yellow magma is let in, the inner drum is started revolving, and the mass heaping against the perforated sides becomes rapidly lighter in color as well as more compact; the syrup flies off, and from the space between the inner and outer drums runs off below into the proper receptacle. The centrifugal is emptied through the bottom of the drums by raising the central spindle and with it the detachable plates around it, so that a circular opening is made in the middle of the apparatus.

A serious loss of sugar in the usual method of working is in the scums, which are frequently thrown away. Professor Wiley, the chemist of the Department of Agriculture, has shown\* that in working a crop of 9063 tons of cane the loss of sugar in the scums, if thrown away, would have amounted to 120,316 pounds, of which 94,545 pounds would have gone in the blanket-scums, and 25,771 pounds in the subsequent scums. To save this sugar, the scums are steamed and then pressed and washed in a filter-press (see p. 157), whereby, practically, the whole of the sugar can be recovered. The scums are generally filter-pressed now in the best Cuban and Louisiana sugar-houses, although a cruder method of pressing them in bags is used on some plantations. The application to cane-juice of the method so generally followed in the case of beet-sugar of adding an excess of lime, which, after the first boiling up, is removed by the process of carbonatation or saturating with carbonic acid gas, has generally been considered to be impossible, because, as was stated before, an excess of lime acts injuriously upon any glucose present and darkens the juice. But if the juice is from sound canes in which the glucose percentage is not large, the advantages of the carbonatation process may exceed the injurious effects. This seems to have been shown by the experiments of the Department of Agriculture at Fort Scott, Kansas, in the fall of 1886.† The yield of sugar in the experiments in which both diffusion and carbonatation

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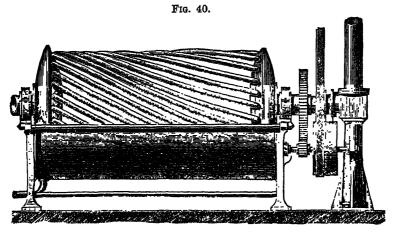
<sup>\*</sup> Bulletin of Department of Agriculture, No. 5, p. 59. † Ibid., No. 14, pp. 52 and 53.

were followed was, as mentioned before, larger than had ever been gotten from sugar-canes. Professor Wiley sums up the advantages of the process as follows: "The process of carbonatation tends to increase the yield of sugar in three ways: (1) It diminishes the amount of glucose. This diminution is small when the cold carbonatation, as practised



at Fort Scott, is used; yet to at least one and a half its extent it increases the yield of crystallized sugar. (2) By the careful use of the process of carbonatation there is scarcely any loss of sugar. The only place where there can be any loss at all is in the press-cakes, and when the desucration of these is properly attended to the total loss is trifling. The wasteful process of skimming is entirely abolished, and the in-

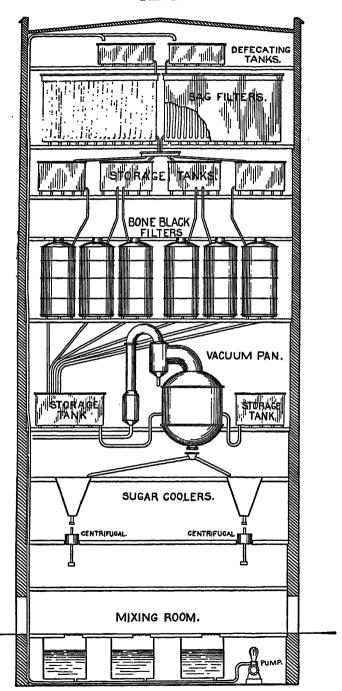
creased yield is due to no mean extent to this truly economical proceeding. (3) In addition to the two causes of increase already noted and which are not sufficient to produce the large rendement obtained, must be mentioned a third, the action of the excess of lime and its precipitation by carbonic acid on the substances in the juice which are truly melassigenic. Fully half of the total increase which the experiments have demonstrated is due to this cause. It is true, the coefficient of purity of the juice does not seem to be much affected by the process, but it is evidence that the treatment to which the juice is subjected increases in a marked degree the ability of the sugar to crystallize. This fact is most abundantly illustrated by the results obtained. Not only this, but it is also evident that the proportion of first sugars to all others is largely increased by this method. This is a fact which may prove of considerable economic importance."



It only remains to notice in connection with raw sugars two forms of apparatus for concentrating raw-sugar juice which have had considerable use in the tropics. The first of these is the "Wetzel pan," an apparatus shown in Fig. 40. As seen, it consists of a pan containing the liquor, in which dip pipes heated by steam passing through them; while the cylinder, formed by these pipes, is caused to revolve by power applied from the end as shown in the cut. The large heating surface enables steam at very low pressure to be used, exhaust steam from the cane-mill engine being sometimes used for the purpose. Such pans are used on some plantations, in the absence of a vacuum-pan, to finish the concentration begun in the battery or copper-wall. The liquor is brought to them at a density of 26° to 27° B. The other form of apparatus referred to is the "Fryer Concretor," in which no attempt is made to produce a crystalline article, but only to evaporate the liquor to such a point that when cold it will assume a solid (concrete) state. The mass is removed as fast as formed, and being plastic while warm it can be cast into blocks of any convenient shape and size, hardening as it cools. In this state it can be shipped in bags or matting, suffering neither deliquescence nor drainage. The "concretor" consists of series of shallow trays placed end to end and divided transversely l ribs running almost from side to side. At one end of these trave is furnace, the flue of which runs beneath them, and at the other end boiler and an air-heater, which utilize the waste heat from the flu employing it both to generate steam and to heat air for the revolving cylinder. The clarified juice flows first upon the tray nearest the fu nace, and then flows down the incline towards the air-heater, meande ing from side to side. While flowing thus it is kept rapidly boiling l means of the heat from the furnace, and its density is raised from about 10° B. to 30° B. From the trays it goes into a hollow revolving cy inder full of scroll-shaped iron plates, over both sides of which tl thickened syrup flows as the cylinder revolves, and thus exposes a ver large surface to the action of hot air which is drawn through by a pa In this cylinder the syrup remains for about twenty minutes and the flows from it at a temperature of about 91° to 94° C., and of such co. sistency that it sets quite hard on cooling.

Raw sugars are often gotten now of sufficient purity to allow of the immediate use without further treatment. Such is not the usual rul however, but they have to undergo a purifying or refining in order bring them to the requisite purity for consumption. The sugar-refinir process is simpler in its theory than the process of preparing the ra sugars, but requires more exactitude in its execution, and more elaboraand costly machinery and equipment. The problem as stated is a muc simpler one than was that of handling the raw cane juice; it is no simply a redissolving of the impure crystalline mass of raw sugar, fre ing the solution from impurities, and then crystallizing afresh the pu sugar from it. The sugar refinery located in a large commercial cent. is almost always a building of considerable height, so as to allow of tl descent by gravity of the sugar solutions from floor to floor as tl process of treatment proceeds. The general outline of the treatment w be easily followed with the aid of the diagram in Fig. 41. sugars as they arrive are discharged from hogsheads or bags in the mixir room on the ground floor through wide gratings into the melting tank or "blow-ups," just below, where boiling water and steam rapidly di solve all that is soluble in the sugars. These tanks hold from three thousand to four thousand five hundred gallons, and treat from nine thirteen tons of sugar at a time. The hogsheads and bags are similar cleaned out by live steam. The crude-sugar solution, run through coarse wire strainer to remove mechanically-mixed impurities, is the pumped to the defecating tanks at the top of the building. The defeca ing is not done, as was the case with raw juice, with lime, but with son form of albumen, as bullock's blood, which, coagulating by the hea encloses and carries with it much of the fine suspended impurities. Fir bone-black is also sometimes added along with the blood. The conten of these defecating tanks are boiled up and agitated thoroughly for fro twenty minutes to half an hour, when the clear liquor is run off in tl troughs leading to the bag-filters. These are of coarse, thick cotte

Fig. 41.

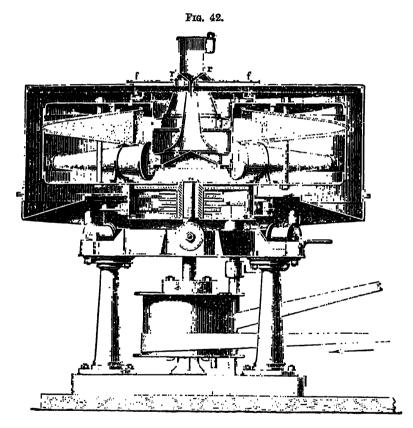


twill, four or five feet long, and but a few inches through. These filte collect the fine suspended slime which would not settle in the defecation tanks. It has been found impossible to replace them by filter-presses the working of the raw cane sugars at present in the market, on accou of the slimy character of the separated matter. The liquor, now co taining soluble impurities only, has a brown color. It goes from t storage-tanks below the bag-filters to the bone-black-filters. These filter immense iron tanks, twenty feet high and eight feet in diameter, opthrough man-holes at the top to the filter-room floor. They have fal bottoms, perforated, over which a blanket is fitted to prevent the bon black flowing through with the liquid. The largest filters hold thir to forty tons of the bone-black. When they are filled with bone-black the man-hole is closed, and the syrup from the cisterns below the ba filters is turned on. It percolates slowly down, is allowed some time settle, and after about seven hours the drawing off begins through narrow discharge-pipe. The filter syrup is caught in different tanks. it becomes deeper in color, and the colorless syrup first obtained used for the finest sugars, and so on. When the charge has run out, the sugars remaining in the charcoal is washed out by running through fresh ( "sweet" water, and the bone-black must be reburned before it ca again be used. From three-quarters to one and a quarter tons of blac are needed per ton of sugar decolorized, according to the quality of the raw sugars. The liquor is now ready to be concentrated in the vacuum pan and brought to the crystallizing point. This vacuum-pan boilir has already been described under raw sugars. The processes of boilin are somewhat different for "mould" and for "soft" sugars. The begrades of syrup boiled to an even, good-sized grain are used for th former, whether loaf, cut, crushed, or pulverized. As the "masse-cuite cools it is run into conical moulds with a small aperture at the bottor or smaller end, through which the uncrystallized liquid may drain of After this has been allowed to drain, water or white syrup is poured i at the top, which washes the crystals as it slowly filters through. After a sufficient time allowed for drainage, the moulds are turned over, s that the small quantity of syrup in the point of the cone shall distribu itself through the mass. The result is the hard white "sugar-loaf," ( conical form of sugar. The process of draining in moulds is, however very generally replaced by the use of large centrifugals, in which sever cones can be dried at a time in a few minutes, saving enormously i time and in the room previously occupied by the large amount of mould needed for several days' working. Such a hydro-extractor for cones shown in Fig. 42. The "soft" sugars, the crystallization of which completed in the cooler after the "masse-cuite" leaves the vacuum-par are cured mostly by centrifugals, and are ready for barrelling on leavin them.

2. Production of Sugar from the Sugar-Beet.—In considering the question of the production of sugar from the sugar-beet, two things must be noticed: first, the soft, pulpy character of the beet, which allow of much more complete extraction of the juice, and, second, the more

complex composition of the juice, which necessitates more elaborate methods of purification of the juice.

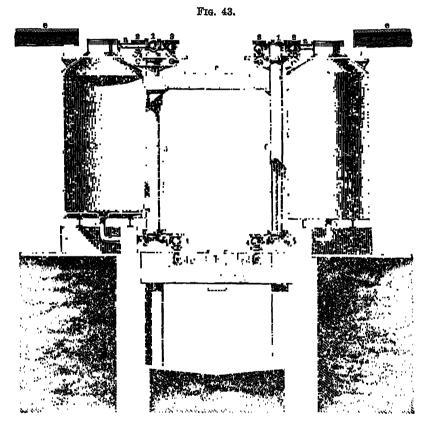
The cultivation and working of the sugar-beet has been developed to so much greater an extent in Germany than any other country that we shall, in describing the extraction of sugar from the beet, notice German methods chiefly. The beets are first washed, brushed and deprived of the tops, and then made to yield their juice by one of four methods: (1) by pulping them and pressing the pulp either in hydraulic presses or between rolls; (2) by centrifugating the pulp; (3) by the maceration



process, in which the pulp is exhausted with either warm or cold water, and the residue pressed; and (4) by the diffusion process, in which the beets are not pulped at all, but are cut into thin transverse sections, known in Germany as "schnitzel," in France as "cosettes," and in English as "chips." These are then put into a series of vessels, in which a current of warm water is made to displace the sugar juice by the principle of "osmosis," or diffusion, as it is more generally called. The first three processes are now almost entirely displaced in Germany by the diffusion process. It is obvious that in this latter the juice will be freer from the fine mechanically suspended impurities and solid particles than in the processes that rupture the cell-walls. In this country the beet-

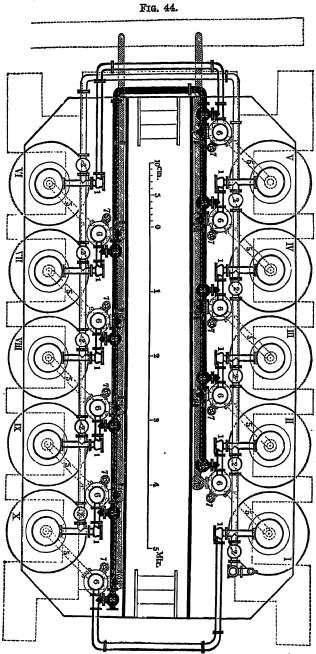
sugar factories have all been equipped with diffusion batteries of approved construction, and that method has been the one exclusively employed. In France the diffusion method has not become so generally popular. As, however, it yields a purer juice and a higher percentage of the same than the older methods, and is, as just stated, the one that is displacing the others, we shall confine ourselves to it.

In the diffusion method of Robert, the fresh beets are cut into slices or "chips" of about one millimetre thickness, which are digested with pure water at from 50° C. to 60° C. This allows the saccharine beet



juice to pass through the cell-walls and mix with the water and the water to replace it in the cells, while the colloid non-sugar remains behind. The vessels used for this diffusion are mostly upright iron cylinders, as shown in Fig. 43, which are provided with a man-hole above for charging them with the chips. A series of these diffusors connected together is known as a battery. They are brought to the proper temperature either by a small steam-coil on the bottom of the vessel or by so-called "calorisators," or juice-warmers, detached upright heating vessels inserted between every two diffusors. A diffusion-battery of ten cells, with juice-warmers, is shown in plan in Fig. 44. From the bottom of each cell, I to X, goes a delivery-tube, 5, to the bottom of the juice-

warmer, where it divides into seven tubes. From the top of each juice-warmer a tube, a, bent at right angles, connects with the next cell. The



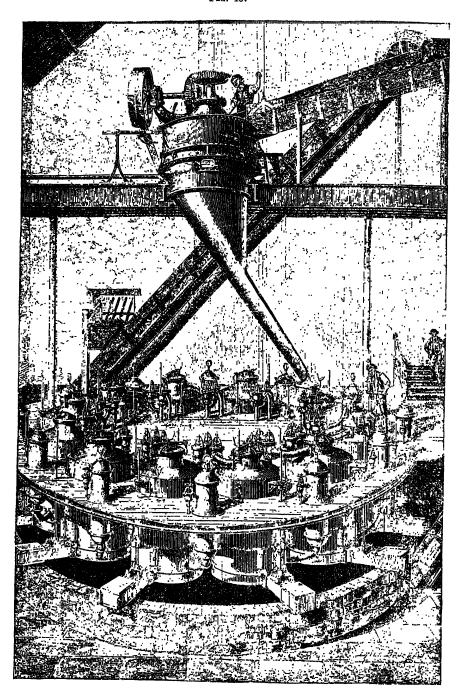
connection of the opposite cells, V and VI, as well as the cells X and I at the other end, is effected, as shown in the ground-plan, by longer

tubes making these bends at right angles. By suitable valves in the supply- and delivery-tubes each cell can be shut off from the others. The upper man-holes of the cells are all reached from the platform e, which runs along just above them; the valves 1, 2, 3 are reached from the platform f, which runs along lower down, supported on cross-pieces, as shown in Fig. 45; and the third platform, g, gives access to the lower valves. A sunken canal, h, in this lowest platform allows of the exhausted chips being discharged from the lower man-holes on to an endless band, which passes around two wheels and delivers them into ascending buckets, whence they go to the chip-press, which dries them. The filling of the cells is effected by means of a swinging trough, not shown in the cut, connecting with a chip-cutter placed on a higher level.

In operating the battery, water at 66° C. is run into the first cell, which has been previously filled with fresh chips. For every cubic metre of space four hundred and fifty kilos, of chips and five hundred kilos. of water are to be reckoned. The cell remains quiet for twenty minutes, during which time the temperature falls to 45° C. The connection with the neighboring juice-warmer is now opened, and the thin juice made to pass into this by forcing fresh cold water into the first diffusion-cell. The juice, brought in the warmer to 66° C., is then passed into the second cell, which has been filled with chips. After twenty minutes the juice in No. 2 is passed into the adjoining juice-warmer, while the cell fills up with the juice from No. 1, and this in turn with fresh water. No. 3, which had been filled meantime with chips, is now brought into the connection. After the juice has been kept in contact, at 66° C., with the contents of each of the three cells in turn for twenty minutes, it is sufficiently concentrated to go to the defecating pan. This juice is therefore sent to be purified, while No. 3 fills up with the thin juice from No. 2. In twenty minutes this is displaced, and, after being warmed to 66° C., goes to No. 4, a freshly-filled cell. After suitable action here it goes direct to the defecating pan, as it is the second diffusate of three cells and the first of a fourth. From this time on, as a new cell comes into operation the juice from one cell goes to the defecating pan until the ninth is in connection, when the first cell is disconnected and emptied of the exhausted chips and then filled with fresh. While this is going on the tenth cell has been connected; and then the second is to be emptied. while the first cell is brought into connection with the tenth. Thus nine cells are always working together in the battery, while the tenth is disconnected for emptying and filling.

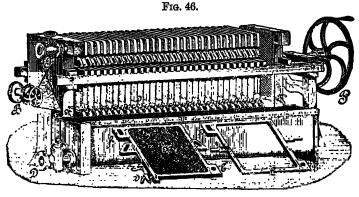
The diffusion-cells are sometimes arranged in a semicircle or a circle instead of a straight line, as this arrangement is thought to be more convenient when the cells are to be filled and emptied. Such a circular diffusion-battery is shown in Fig. 45, and the method of filling the cells with the chips or slices is shown, as well as the endless belt carrying up the buckets of exhausted chips to be emptied. A continuous diffusor, consisting of one long cell, in which the chips and water move in opposite directions, so that as the juice becomes more concentrated it shall meet chips richer and richer in sugar, has also been devised.

Fig. 45.



As stated, the percentage of extraction by these methods is higher and the juice is purer than by any other method, while the dried chip also serve as most valuable fertilizer material or for cattle food. The average composition is: ash, 5.67; fat, .49; crude fibre, 23.36; crude protein, 8.70; and non-nitrogenous extractives, 61.78. A modification of this diffusion process by Bergreen, already found advantageous in practice, is to exhaust the cells of air after filling them with fresh beet-chip and then to allow expanded steam to enter, so as to coagulate the albuminoids. The usual procedure then follows. The exhausted chips gotte thus make good cattle food, as they are richer in nitrogenous matter.

The beet juice, by whichever of the four methods heretofore method it may be gotten, is now to be purified. The general outline the method of working up the juice is shown on the accompanying diagram, based on that of Post,\* but modified to accord with recent in provements. Except in the case of the diffusion juice of Bergreen process mentioned above, the crude juice is heated by indirect steam 80° C. to coagulate the albuminoids, and then two to two and one-ha



per cent. of caustic lime, in the form of milk of lime, is added. lime saturates the free acids and throws out nitrogenous compounas in the case of cane juice, and, because of its excess, forms solut calcium saccharates with some of the sugar. Carbonic acid gas is the added until the precipitated carbonate of lime becomes granular ar settles readily. At this time there still remains a slight excess of fr lime,—about .1 to .2 per cent. The contents of the saturation-pan a now pumped into the filter-presses and the press-cakes washed free fro sugar by steam. A filter-press, such as is adapted for sugar-scums ar carbonatation press-cakes, is shown in Fig. 46. This treatment is calle the first carbonatation. The juice may be filtered now at once through bone-black, which will withdraw the remaining lime as well as dece orize it, but in most German sugar-houses it is subjected, boiling hot. a second treatment with one-half per cent. of lime, and then complete neutralized with carbonic acid. This is called the second carbonatatic or the saturation. After again going through the filter-press the jui

<sup>\*</sup> Post, Chemische Technologie, ii, p. 274.

goes to the bone-black-filters. In many of the newer German sugar-houses the filtration of the thin juice through bone-black is no longer practised, as repeated saturations with lime and carbonic acid or treatment with sulphurous acid and sulphites have so clarified it as to make bone-black unnecessary. It is stated that at Watsonville, California, in the beet-sugar factory of Spreckels, bone-black filtration is thus dispensed with. The thin filtered juice is concentrated in double or triple effect vacuum-pans to 24° or 25° B., and then filtered again as thick juice through bone-black. This second filtration takes the last traces of nitrogenous materials out, and the remnant of lime which remained in solution. It is then concentrated in the vacuum-pan to crystallization.

In the preparation of raw sugar, the "masse-cuite" is dropped from the vacuum-pan into small coolers of about two hundred kilos. capacity, in which it becomes cold and crystallization is completed. The contents of these coolers are then mixed and broken up and rubbed to a paste with the aid of some syrup, and the whole centrifiguated. The sugar so obtained is the raw beet-sugar of commerce. The syrup obtained is concentrated in a vacuum-pan, and the sugar from this forms the second product, which sometimes goes into commerce and sometimes is returned to the thick juice to be worked up with it.

As was stated before, raw cane-sugar can be obtained by care and with the best vacuum-pan practice so nearly pure as to be directly available for use without any special refining. In the case of raw beet-sugar this is much more difficult. The raw beet-sugar, though it may be well crystallized, usually contains substances of decidedly unpleasant odor and taste, chiefly decomposition products of the betäine of the juice (see composition of the beet, p. 136), which are in the syrup adhering to the crystals.

As end-products from 100 kilos. of beets containing sixteen per cent. of sucrose, are obtained:

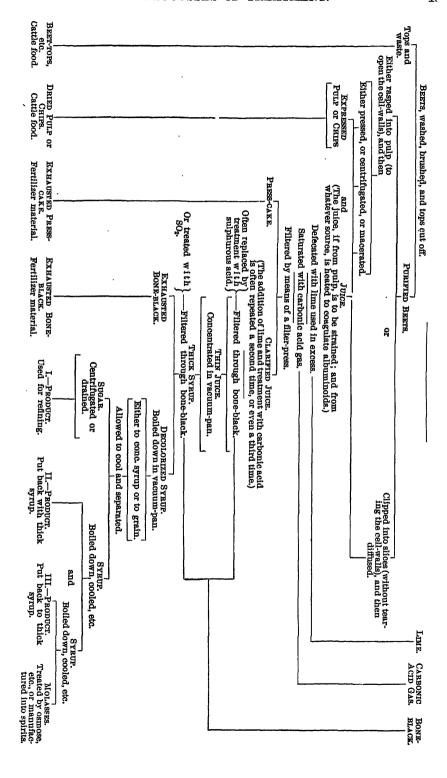
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13.5 kilos of raw beet sugar I., containing
1.0 kilo of secondary product, containing
2.2 kilos of molasses, containing

13.5 kilos of raw beet sugar I., containing
13.6 kilos of secondary product, containing
13.6 kilos sucrose.
13.9 kilos of secondary product, containing
13.6 kilos sucrose.
13.7 kilos of secondary product, containing
13.6 kilos sucrose.
13.6 kilos of secondary product, containing
13.6 kilos sucrose.
13.7 kilos of secondary product, containing
13.7 kilos sucrose.
13.8 kilos sucrose.
14.98 kilos sucrose.
```

There are obtained, in addition, six kilos. of dry beet chips and ten kilos. of separated scums.

The production for direct consumption of a commoner sugar, known in Germany as "melis," or lump-sugar, is an important branch of the raw sugar-making. In this case the contents of the vacuum-pan brought to grain, but without the special building of crystals, are discharged into shallow vessels with false bottoms, which may be called "warmers," in which the "masse-cuite" is heated up from 60° to 90° C., which has the effect of redissolving most of the small crystals. The warmed syrup is now filled into the moulds, in which it crystallizes uniformly to a compact whole. This grade of sugar would have as so produced a light yellow color, which is usually corrected by the addition of ultramarine blue.

Of course, raw beet-sugars can be most advantageously purified by a complete refining process, analogous to that described under cane-sugar,



in which they are redissolved, clarified, decolorized, and again crystalized. The procedure is so similar to that described under the refining of cane-sugar that it need not be specially noticed here.

3. The Working up of the Molasses.—It is stated in the tabular view of the working of cane-sugar on p. 140 that the molasses is used for syrup or worked over into molasses sugars. We should distinguish, however, between the several grades of molasses. In working up the raw sugar reference was made to first, second, and third sugars. Corresponding to each of these three grades, of course, is a different molasses, sometimes known as first, second, and third molasses, and sometimes as second, third, and fourth molasses. The average percentage of sucrose and of reducing sugars in these is shown from the analyses of the United States Department of Agriculture\* made at Magnolia, Louisiana, in 1884.

First molasses ... Sucrose, 37.97 per cent.

Second molasses ... Sucrose, 41.23 per cent.

Third molasses ... Sucrose, 21.87 per cent.

Reducing sugar, 8.13 per cent.

Reducing sugar, 18.32 per cent.

Reducing sugar, 21.06 per cent.

The percentage of solid, non-sugar in the first and second of these molasses will nearly, if not quite, equal that of the sucrose, while in the third it considerably exceeds it.

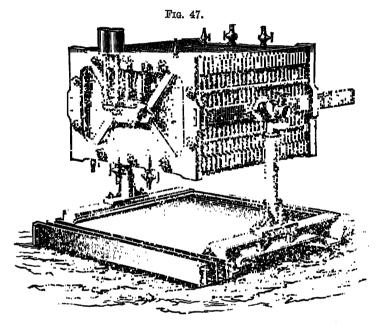
The "first molasses" is sufficiently pure to be mixed with syrup sugar in the pan for the production of a second product sugar; the "second molasses" can be refined as such for brown or grocery sugars, and the "third molasses" is so sticky and impure that it can only be sent to the rum-distillery, where it is fermented for rum. (See p. 219.)

With respect to beet-root molasses the case is different. It is very impure from mineral salts and nitrogenous materials, but is nearly pure from the invert or reducing sugar so abundant in cane-sugar molasses. and in recent years it has been found possible to work it specifically for the extraction of the sucrose, of which over ninety per cent. is now extracted, thus reducing the loss of sugar to a minimum. The average composition of beet-sugar molasses is given at fifty per cent. of sucrose, thirty per cent. of non-sugar, and twenty per cent. of water. Of these thirty non-sugar, ten are made up of inorganic salts, chiefly potash compounds, and twenty of organic non-sugar (see composition of the sugarbeet, p. 136). As the amount of beet-sugar molasses produced in Continental Europe annually is estimated at 450,000 tons, the fifty per cent. of sucrose represents 25,000 tons of sugar which it was certainly desirable to extract if possible. The processes for accomplishing this depend upon either one or the other of two principles: either to withdraw from the molasses the potash and other mineral salts which prevent the crystallization of the sucrose, or to precipitate out the sucrose in combination with calcium or strontium as an insoluble sucrate, which is then mixed with water and decomposed by carbon dioxide or used in the defecation of beet juice instead of lime.

The elimination of the potash salts may be effected, according to

<sup>\*</sup> Bulletin No. 5, p. 52.

Newland's proposal, by the addition of aluminum sulphate so as to for potash alum, which is crystallized out, or by the "osmose" process, which the principle of diffusion already referred to (see p. 152) is aga made use of. In this case advantage is taken of the fact that the potassalts are the most crystalline constituents of the molasses, and hence we pass through a sheet of vegetable parchment more rapidly than the oth constituents. So if the molasses warmed to 80° or 90° C. be made pass in a stream on the one side of such a membrane while pure wat passes on the other, the potash salts diffuse through, and are to the degree eliminated from the molasses. However, the difference in the rapidity of diffusion of the salts and the sucrose is not sufficiently gre



to allow of a very perfect separation, so that to avoid loss of sugar to operation must be stopped before the elimination of salts is complete. little more than half of the sugar can be recovered from the molasses this way. The apparatus in which this treatment of the molasses carried out is known as an osmogene, and is illustrated in Fig. 47. consists of a number of very narrow but high and deep cells adjoining each other, the sides of which are of parchment paper. Through alternate cells in this system goes the heated molasses, and through the intevening cells the water at the same temperature, each connecting will lateral canals for the supply and withdrawal of the respective liquid. The ordinary osmose apparatus of the German sugar-houses is capalt of working 1000 kilos. or upwards of molasses per day, and at a cost 1.60 marks (38.4 cents) per 100 kilos. of molasses. The osmose sugar somewhat darker in color than ordinary second or third sugar, but of pleasanter and sweeter taste. The yield of the osmose process vari

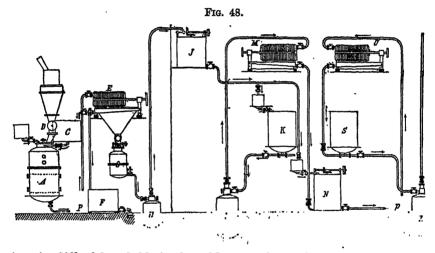
with the grade of the molasses taken; a molasses with a purity coefficient of fifty-eight to sixty will yield ten to twelve per cent. of the molasses taken, and one of a coefficient of sixty to sixty-five will yield seventeen, or sometimes as high as twenty, per cent. By repeating the osmose process thrice the yield can be raised to thirty per cent. out of the possible fifty per cent. of sucrose contained in the molasses.

Of the methods depending upon the formation of a lime or strontia sucrate, the most important are the Scheibler-Seyferth elution process, the Steffen substitution and separation processes, and the strontium processes.

In the first of these processes, finely powdered quicklime is added to the molasses, which has been previously concentrated in vacuo to 84° to 85° Brix, in the proportion of about twenty-five parts of the former to one hundred parts of the latter. The lime slakes at the expense of the water of the molasses, and leaves the tribasic calcium sucrate in the form of a dry porous mass. This is then broken up and put into the "elutors." vessels which are somewhat similar in design to the cells of a diffusionbattery. The impure sucrate is here systematically washed with thirtyfive per cent. alcohol, which dissolves away from it most of the adhering impurities. The washed sucrate is then brought to the condition of a fine paste with water, and either decomposed with carbon dioxide or used instead of lime in treating fresh beet juice. This process takes out eighty-five to ninety per cent. of the sugar contained in the molasses, but the cost is somewhat greater than in the case of the osmose process. The alcohol is recovered from the washings by distillation. Steffen's substitution process depends upon the difference in solubility of the tricalcium sucrate at high and low temperatures. The molasses is first diluted so that it shall contain about eighty per cent. of sugar, and then caustic lime added until some two to three per cent. has been used. The whole mass is then heated to 115° C., when the tricalcium sucrate is precipitated and separated by the use of a filter-press. The sucrate is ground up. again filter-pressed, and then can be used in defecating sugar juice. The washings from the filter-press are used to dilute a fresh quantity of molasses to the degree mentioned before, which, treated with lime in the proper proportion and heated up, separates the sucrate, which is treated as before. After about the twentieth operation, the cooled motherliquors and wash-waters are treated with lime alone, and the residual liquors after this treatment are then rejected. In the Steffen separation process, on the other hand, the molasses solution is kept cold, the temperature not being allowed to rise over 30° C. (86° F.). The molasses is diluted until the density shows 12° Brix, the percentage of sugar being then from seven to eight. This solution is cooled down to 15° C. (59° F.), and finely-powdered quicklime is added in small portions at intervals of about a minute, the temperature rising a little each time and being again cooled down. The mixing of the molasses and the lime, in the proportion of fifty to one hundred of powdered lime, according to quality, to one hundred of dry sugar, in the solution takes place in a closed mixing-vessel of iron provided with tubes through which cold

water is kept circulating, and with a mechanical agitator to mix t contents uniformly. The insoluble sucrate separates out rapidly in t cold, and the contents of the mixer A (see Fig. 48) are pumped to t filter-press E, where the sucrate is washed, the mother-liquor, containing all the impurities of the molasses, being put aside for fertilizing purposes, the wash-water, however, being collected in F for use in diluting new quantities of molasses. The washed sucrate drops from the filter press into the sucrate-mill G, where it is mixed to a thin paste wing water, and then pumped, by means of the monte-jus H, to the receptate J. From here it can be sent into the first saturation-vessel K, and the filter-press M, and to the second saturation-vessel S, and the filter press O.

The process which at the present time is most favorably regarded as which recovers the highest percentage of sugar is the strontium proces. In this the sugar is precipitated either as monostrontium sucrate, which



is quite difficultly soluble in the cold, or as bistrontium sucrate separatir from hot solution. According to Scheibler's monosucrate procedure, tl molasses is well mixed with hot saturated strontium hydroxide solution and the mixture passed over cooling apparatus into crystallizing tank where a few crystals of the monosucrate are added to start the crystall zation. After some hours the whole mass is changed into a crystallir magma, which is broken up and put through a filter-press. The whicakes of strontium sucrate go, as in the case of calcium sucrate, to the treatment of crude beet juice, while the mother-liquor is treated wit more caustic strontia and boiled, when bistrontium sucrate is precip tated. This is dense enough to be washed by decantation, and then can k used instead of strontia solution with fresh molasses for the formatio of monostrontium sucrate. The excess of strontia is recovered from a the mother-liquors and worked over into caustic strontia. By the other strontium process the molasses is added to a twenty-five per cent. stron tium hydroxide solution, both taken hot, in such amount that for one par

of sugar about two and one-half parts of strontium hydroxide are present. The precipitated bistrontium sucrate separates rapidly, and the mother-liquor can be decanted from it. The sucrate is washed with hot water or with a ten per cent. hot strontium solution. In order to decompose the sucrate, it is brought in a refrigerating chamber and cooled to 10° to 12° C., when, after twenty-four to seventy-two hours' standing, according to temperature, etc., it decomposes into crystallized strontium hydroxide and sugar solution, containing something less than half of the strontia. After filtering off the crystallized strontium hydroxide, the sugar-liquor is decomposed with carbon dioxide in the usual way.

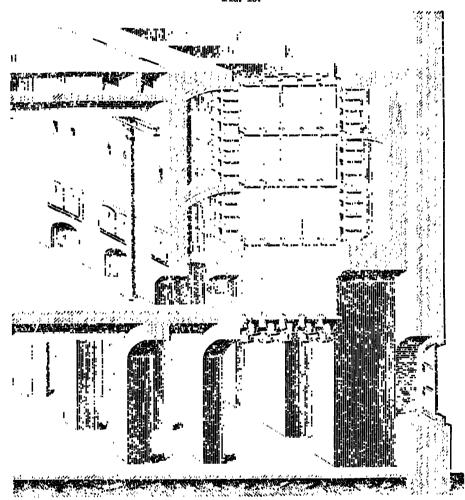
In Germany in 1891–92, 48 sugar-houses extracted by the osmose process, 28 by the elution and precipitation process, 3 substitution, 20 separation, and 1 strontium process. In 1906, out of a total amount of 222,670 tons of molasses worked for sugar extraction, 210,560 tons were worked by the strontium process and most of the rest by the lime "separation" process.

4. REVIVIFYING OF THE BONE-BLACK.—The bone-black, or "char," after use in the filters, becomes charged with impurities and loses for the time its decolorizing power. It can, however, be restored to activity, or "revivified," by suitable treatment so as to be used again for filtration, and this process can be repeated many times before, by the gradual loss of its porous character and change of composition, it becomes unfit for use. In working sugars from the cane this revivification is a much simpler process than in the case of beet-sugars. In the former case, water as hot as possible is run in at the top of the filter, which displaces the sugar solution remaining in the pores of the char and forms a dilute solution of sugar and the soluble impurities taken up from the liquor. This dilute solution is known as "sweet-water," and is usually boiled down in triple effects and run in with the lower-grade products. After running additional hot water through, the filters are drained, and the moist char, after a partial drying, is put into the top of the vertical retorts, in which it is to be heated out of access of air for the decomposition of the organic matter still remaining in the pores and the restoration of its absorbent power. Various forms of char-kilns are in use in different refineries. That shown in Fig. 49 represents one of the simpler forms of char-kilns. The moist spent black from the filters in which it was washed goes on to the floor H, where it is dried by the waste heat passing through G and F, and then goes into the openings at J, which are kept always heaped up. The black descends in the retort-pipes A from the upper cooler portions into the middle hottest part, and then, as portions are withdrawn below, into a cooler section again. The black drawn off below is protected from the air by being received into closed receptacles or at once filled into the bone-black-filters. In other forms of kilns, the retorts are rotated slowly by mechanism so as to heat all parts equally.

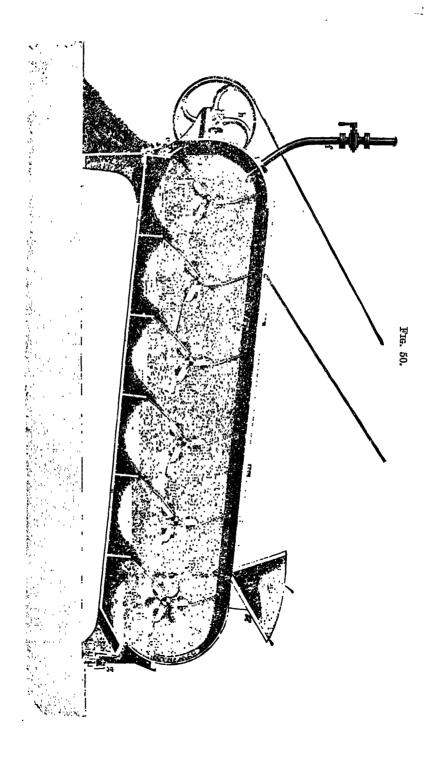
In beet-sugar refineries the revivifying of the char, as before stated, is a more tedious process. This is in part because the juices and syrups have been limed in such excess in the preliminary stages of treatment,

and in part because the beet juice contains much more albuminoid and organic non-sugar, which is absorbed in the pores of the char and cannot be gotten rid of by simple washing. The first step in the revivifying, then, in this case, is a treatment with a calculated amount of hydrochloric acid to remove the excess of carbonate of lime; after this a thor-





ough washing of the black in special washing-machines, such as the Klusemann washer, shown in Fig. 50; then a fermentation to decompose into simpler and soluble constituents the absorbed albuminoids and other organic matter. The fermentation may be either what is termed the dry fermentation, in the presence of a very small quantity of water, or the moist fermentation in the presence of a larger amount. The first takes from twelve to twenty hours, while the latter requires from six to seven hours only. The black, after the fermentation, is treated with



boiling alkaline solutions, washed, and then burned in char-kilns already described. The char seems to improve in filtering power at fir as a consequence of revivifying, but soon loses again and runs dov steadily in value. This is in large part due to the separation out in t pores of carbonized residue from the burning. This carbon has no d colorizing power like the nitrogenized carbon of the original bone-blac but simply clogs the pores of the char and mechanically obstructs i action.

A new process of Soxhlet whereby a mixture of fine ground wood fib and infusorial earth is added to the solutions before filter-pressing h produced such clear filtrates that the use of bone-black is largely d pensed with even in refining the raw beet-sugar.

## III. Products of Manufacture.

1. RAW SUGARS.—The composition of the juice from both the sugar cane and the sugar-beet has been stated, and the processes for preparit the raw sugar from each of these sources. We may now examine mo closely the character of the products obtained. The raw cane-sugamade as it is chiefly in the tropics under a variety of conditions of woring, from the most primitive to the most highly improved, has come in commerce under a great variety of names as well as of varying grades purity. The raw beet-sugar is usually known as first, second, or this product sugar. (See p. 158.)

Muscovado is a brown sugar produced in the West Indies, general by open-pan boiling, which has been drained in hogsheads or perforate casks, and so freed in large part from the accompanying molasses.

Concrete, or concreted sugar, is the product of the Fryer concret (see p. 148) or similar form of apparatus, and is a compact, boiled-dow mass, containing both the crystallizable sugar and impurities which or narily go into the molasses. It shows little or no distinct grain.

Clayed sugars have been freed from the dark molasses by coverir them in moulds by moist clay, which allows of a gradual washing ar displacement of the adhering syrup.

Bastards is the name given to an impure sugar gotten by concertrating molasses and allowing to crystallize slowly in moulds.

Jaggery is the name given to a very impure East Indian palm-suga sometimes refined in England, but chiefly consumed in the country of i production.

Demerara crystals are the product of the best vacuum-pan boilir and have been well purged in the centrifugals. They have the lig! yellow bloom due to treatment with sulphuric acid. (See p. 146.)

These Demerara crystals have also been brought to the United Stat with very dark brown color. This, however, was only superficial, ar was capable of removal by centrifugating with a lighter-colored syru. The dark color was imparted like the yellow bloom by the action of suphuric acid added in the vacuum-pan before discharging the contents of the same.

The composition of a variety	of raw	cane-	and	beet-sugars	is	given	in
the accompanying table:						_	

DESCRIPTION OF SUGAR.	Sucrose.	Glucose.	Organic non- sugar.	Ash.	Water.	Authority.
Cane, Cuba (centrif.)  " Cuba (muscovado)  " Jamaica " Trinidad " Porto Rico " St. Vincent " Demerara " Benares " Unclayed Manila " Concrete " Melada " Bastards Palm East Indian Beet, First product " Second product	91,90 92,35 90,40 88,00 87,50 92,50 90,80 94,50 84,20 67,00 68,30 86,00 94,17 91,68	2.98 3.38 3.47 5.14 4.84 8.61 4.11 2.68 6.79 8.45 11.36 15.00 2.19	2.70 0.66 1.55 1.67 2.60 2.45 0.77 0.89 8.24 1.70 1.98 1.20 2.89 2.14 2.49	0.72 0.77 0.36 0.96 0.81 0.63 1.12 1.50 2.00 1.10 0.91 1.50 2.88 1.48 2.92	1.70 2.84 4.22 4.23 4.25 0.81 3.20 0.98 5.97 4.55 18.80 14.00 6.04 2.21 2.91	Wigner and Harland. Wallace. Wigner and Harland. Wigner and Harland. Wallace. Wallace. Wallace. Wallace. Wigner and Harland. Bodenbender. Bodenbender.

2. Refined Sugars.—The commercial designations of refined sugars are very varied. We may distinguish in general between hard sugars and soft sugars, the former of which are more thoroughly and carefully dried by the aid of artificial heat, while the latter are merely centrifugated, and so retain from three to four per cent. of water in the traces of syrup adhering to the sugar. To the former class belongs sugar "crystals," or sugar in well-formed individual transparent crystals, which are as pure as rock-candy, as well as loaf-sugar in the forms of pulverized, crushed, granulated, and cube sugars. To the latter belong what are called grocery sugars, of which the finest grades are called A sugars, the next B sugars, and so on.

In Germany the finest white beet-sugars are known as "raffinade," inferior grades as "melis" (or Brodzucker), as "pilé," and as "farin," the last of which is of inferior grain and color.

The hard sugars in general all show a sucrose percentage of ninetynine or over, while the soft cane-sugars and the second grade beet-sugars show from ninety-six to ninety-eight per cent.

3. Molasses and Cane-sugar Syrups.—The molasses may be termed the mother-liquor of the crystallized product, the sugar. It is never found possible in practice, however, to crystallize all the sugar out or to get a molasses which shall not contain sucrose. The potash salts, and in a lesser degree the calcium salts, which are present in the crude juice are "melassigenic,"—that is, prevent the crystallization of a certain amount of the sucrose; the invert sugar, or glucose, operates in the same way, and the long-continued heating of the sugar solutions also has the effect of increasing the molasses. In France, for instance, the rendement, or amount of crystallized sugar obtainable in refining of raw sugars, is calculated by deducting from the total sucrose twice the glucose, and from three to five times the ash. In the case of cane-sugars the ash is not so melassigenic, not being so largely composed of potassium compounds as with the beet, and a deduction of one and a half times the glucose is considered sufficient to allow for the impurity.

The experience during some years with sorghum-sugar, as manufactured by the United States Bureau of Agriculture and several sorghum-sugar factories in Kansas, has shown that this rule does not apply to sorghum. Professor Swenson, the chemist of the Parkinson Company at Fort Scott, Kansas, found that in the case of sorghum juice the glucose and other solids, known as "non-sugar," prevent only two-fifths of their weight of cane-sugar from crystallizing, so that in the season of 1887, instead of there being only 61.6 pounds available sugar per ton of cane worked as the analyses indicated according to the old rule, as a matter of fact, 130.5 pounds were obtained.

But with the sugar-cane and the sugar-beet the percentage of sucrose, in both the raw molasses produced in the extraction of the sugar from the juice and "refined molasses," the syrup produced in the process of refining, is quite large. The composition of the first, second, and third molasses of the Louisiana cane-sugar plantation has already been given (see p. 160), as well as the average composition of beet-root molasses. The following analysis of a variety of molasses will further illustrate the differences in the several grades:

	Sucrose.	Glucose.	Ash.	Organic non- sugar.	Water.	Authority.
From sugar-cane: Green syrup Golden syrup Treacle West Indian molasses Dark molasses From beets:	62.7 89.6 82.5 47.0 85.0 46.7 50.0 55.0	8.0 33.0 37.2 20,4 10.0 0.6 	1.0 2.5 3.5 2.6 5.0 18.2 10.0 12.0	0.6 2.8 3.5 2.7 10.0 15.8 20.0 13.0	27.7 22.7 28.4 27.3 20.0 28.7 20.0 20.0	Wallace. Wallace. Wallace. Wallace. J. H. Tucker. Wallace. Wigner and Harland. J. H. Tucker.

It will be seen from these analyses that the percentage of sucrose is usually much higher in the beet-root molasses, which is explained by the large percentage of ash and organic non-sugar. On the other hand, the glucose, or invert sugar, is large in the cane-sugar molasses, but almost entirely wanting in the beet-sugar molasses. The latter, however, always contains raffinose, another variety of sugar always present in the beet juice, betäine, a nitrogenous base, and proteids. The proportion of salts contained in beet-root molasses is usually ten to fourteen per cent., whereas refiner's molasses from cane-sugar rarely contains half that proportion.

The term green syrup, used above, is given to the syrup centrifugated from the second products in the refining process.

Golden syrup is produced from a refiner's molasses by diluting, filtering through bone-black, and then concentrating.

Treacle is the name formerly given to the drainings from the dark molasses sugars called bastards. (See p. 167.)

Cane-sugar molasses, when refined and brought to the condition of light-colored syrups, forms a common article of domestic consumption

under the general name of table syrup. The table syrups of the present day, however, cannot, as a rule, claim to be simple products of the refining process, as they are almost always largely admixed with the cheaper glucose syrup, and the cane-sugar product in them is often entirely replaced by this latter. A glucose product, known as "mixing syrup," is quite openly sold for this purpose.

Beet-sugar molasses is not adapted for use as table syrup on account of the unpleasant taste and odor, due to the nitrogenous principles present. It is, as before described, worked for the extraction of the sugar, or it is fermented for alcohol.

4. Miscellaneous Side-products.—(1) Exhausted Residue from the Sugar-cane or Sugar-beet.—The character of this residue differs very greatly according to the method of juice extraction which has been followed. The common sugar-cane residue from the roll-mills, known as "bagasse," consists of the fibre and cellular material of the cane still enclosing some six per cent. of sucrose, or about one-third of the total eighteen per cent. which the fresh-cut cane contains. It is very largely used as fuel on the sugar plantations, and the ash serves to some extent as fertilizing material for the soil. The cane-fibre, when freed more fully from the sugar by the diffusion process, has been proposed as a source of paper-stock. (See p. 140.)

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Both the pressed pulp and the exhausted diffusion-chips from the sugar-beet are recognized as valuable cattle food. Märcker found in the dried press-cake 1.227 per cent. of nitrogen. The exhausted chips of the diffusion-cells are still richer in nitrogen, as the diffusion process does not extract as much nitrogenous matter as the method of crushing.

(2) Scums and Saturation Press-cakes.—In describing the production of raw cane-sugar mention was made of the scums, which had at one time been thrown away, but which when filter-pressed yielded a very considerable additional amount of sugar. The press-cake obtained in this treatment has also a value. It contains on an average as taken from the press 45.17 per cent. of water, 15.67 per cent. of ash, 3.49 per cent. of phosphoric anhydride, and 1.14 per cent. of nitrogen, or, reckoned on the dry material, 28.56 per cent. of ash, 6.33 per cent. of phosphoric anhydride, and 2.10 per cent. of nitrogen. Its value, as taken from the press, at the ruling rates for fertilizing materials, would be \$10.64 per ton.\* Where the carbonatation process is used, and the excess of lime removed by carbon dioxide, the scums and carbonate of lime are found together in the press-cake gotten by filtering. In the experimental tests of the carbonatation process as applied to cane-sugar made by the United States Department of Agriculture at Fort Scott, Kansas, in 1886,† the press-cake obtained after saturation and filtering when dried was found to contain 9.585 per cent. of albuminoids and 17.45 per cent. of other organic matter. The saturation press-cake of the beet-sugar process does not contain so high a percentage of albuminoids, but a much

<sup>\*</sup> Bulletin of Department of Agriculture, No. 11, p. 16. † Ibid., No. 14, p. 54.

larger amount of nitrogenous compounds remains in the clarified juic giving rise to the escape of ammonia on concentration in the vacuum-pa and showing itself in the molasses.

(3) Exhausted Bone-black.—The bone-black after repeated revivifing (see p. 164) becomes at last valueless for filtration purposes at passes out of the sugar-refinery, going to the manufacturer of fertilizer for whom it is a very valuable material. The more calcium phospha and the less calcium carbonate it contains, the more valuable it is f superphosphate manufacture, as, on the addition of sulphuric acid, the liberated phosphoric acid remains, adding to the value of the production an average thirteen per cent. of calcium carbonate, sixty to sevent four per cent. of calcium phosphate, four per cent. of carbon, and foutenths to six-tenths per cent. of nitrogen.

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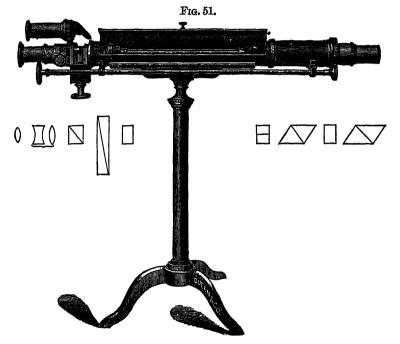
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(4) Vinasse, or Molasses Residues.—When the beet molasses is fe mented for the production of alcohol, the residual liquor, which contain all the potash salts of the molasses, is known in French as "vinasse." in German as "schlempe." It is of about 41° B. and acid in reaction It is neutralized with calcium carbonate and then evaporated down dryness and calcined. The black porous residue so obtained contain thirty to thirty-five per cent. of potassium carbonate, eighteen to twent per cent. of sodium carbonate, eighteen to twenty-two per cent. of pota sium chloride, six to eight per cent. of potassium sulphate, and fifted to twenty-eight per cent. of insoluble matter. It is exhausted with he water, and the extract evaporated down, when potassium sulphate an afterwards sodium carbonate separate out. On cooling, potassium chl ride and potassium sulphate crystallize out, and the mother-liquor con tains potassium carbonate admixed with some sodium carbonate. It possible by this gradual evaporation and fractional crystallization 1 bring the crude potashes to a purity of ninety per cent. In this produ tion of the solid potashes from the molasses residue all the nitrogen of the molasses is lost. To prevent this, C. Vincent, a French chemist, he proposed to submit the evaporated vinasse to a dry distillation instea of calcination in the air. The residue of this distillation is an open an very porous coke containing all the mineral salts of the molasses, which can then be extracted as before. The products of distillation are a illuminating and heating gas, ammonia water, and a small amount c The ammonia water is the most interesting product. It contain besides carbonate, sulphide and cyanide of ammonium, methyl alcoho and notable quantities of trimethylamine. This latter can be decompose at 320° C. by dry hydrochloric acid gas into methyl chloride an ammonia, and on passing the products through aqueous hydrochloric acid the methyl chloride goes through unabsorbed, while the ammonia taken up. The methyl chloride is of great value for ice machines an for the manufacture of methylated aniline colors. (See p. 457.) process was quite largely introduced, but as in recent years the molasse is worked over for sugar in increasing amounts, less molasses is fer mented, and hence less vinasse is obtained.

## IV. Analytical Tests and Methods.

1. Determination of Sucrose.—(A) Optical Methods.—Among the most important physical properties of many of the varieties of sugars is the power possessed by their solutions of rotating the plane of polarization to the right or the left. They are accordingly classified as dextrorotatory, levo-rotatory, or optically inactive in case no power of circular polarization is manifested. This property as possessed by solutions of cane-sugar, of deviating the polarized ray in a fixed and definite degree, has been made the basis of the method of analysis by means of polariscopes. The fundamental idea involved in these instruments is to compensate for and so determine the optical rotatory power of sugar solu-

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tions of unknown strength by the corresponding circular polarizing action of quartz plates of known thickness, and hence of known power. The earliest of polariscopes was the Mitscherlich instrument, but those now in use for sugar analysis are either the Soleil-Ventzke-Scheibler, the Soleil-Dubosq, the Laurent shadow instrument, or the Schmidt and Haensch, which last claims to combine the best features of the Soleil and the Laurent instruments. A general view and a longitudinal section of this instrument is given in Fig. 51. The glass tube containing the sugar solution is shown lying in the axis of the telescope and the polarizing prisms. To the right below is shown the polarizing prism (the so-called Jellet-Cornu prism), to the left is the analyzing prism, a quartz plate, quartz wedges of opposite rotatory power, and the lenses of the telescope, with a plate of bichromate of potash to correct for any color in the field.

In this instrument, which uses white light, the field of view is a circle, which, with the instrument at 0° and nothing intercepting the light, is of a uniform gray tint. When a sugar solution is interposed, one-half of the circle becomes darker than the other, and the quartz wedges, controlled by the screw shown underneath, must be moved to compensate for the rotation due to the sugar solution and to restore the uniformity of tint. The instrument is so graduated that one degree of displacement on the scale corresponds to .26048 gramme of cane-sugar dissolved in 100 cubic centimetres of water and viewed through a 200-millimetre tube. Therefore 26.048 grammes of the sugar to be analyzed are weighed out. If chemically pure and anhydrous, the solution of the strength stated should read one hundred degrees of displacement, or one hundred per cent. of sugar, and if impure, correspondingly less.

In the application of polariscope analysis to cane-sugars two cases may arise: first, when no other optically active substance is present, and, second, when glucose or invert sugar is also present.

- (a) Absence of other Optically Active Substances.—The weighed sample is dissolved in about fifty cubic centimetres of water in a flask marked for one hundred cubic centimetres. As soon as the sugar is all dissolved, a few cubic centimetres of a solution of basic acetate of lead are added, and two or three cubic centimetres of cream of hydrated alumina. The liquid is well agitated, and then the flask is filled nearly to the mark on the neck with water and the froth allowed to rise to the surface, when it is flattened by the addition of a drop of ether. Water is now added exactly to the mark, the contents of the flask thoroughly agitated, and the liquid filtered through a dry filter. In the case of very dark sugars, purified and perfectly dry bone-black has been added for clarifying purposes. However, it is generally acknowledged to introduce error by its absorption of small amounts of sugar, so that it is now dispensed with, or if used on the dry filter, the first third of the filtrate is rejected and the later portions only used. Allen\* recommends instead the use of a ten per cent. solution of sodium sulphite. The tube of the polariscope is now rinsed with the clear sugar solution and then filled with the same, the open end closed with a smooth glass plate held in place by a brass cap, which is screwed on. The tube containing the sugar solution is then placed in the instrument, and the lower thumbscrew turned until the uniformity of shade in the two halves of the field is restored, when the number of degrees (or percentage of cane-sugar in the sample) is read off on the scale.
- (b) Presence of Glucose, Invert Sugar, or other Optically Active Substance.—The action of acids upon cane-sugar has already been stated to cause inversion,—i.e., change of the sucrose into dextrose and levulose. Both these varieties of sugars differ from sucrose in their optical power. If, then, these alteration products accompany the sucrose in a cane-sugar sample, the results of the polariscope reading may be vitiated. Some writers have held that the invert sugar present in raw

<sup>\*</sup> Commercial Organic Analysis, 3d ed., vol. i. p. 257.

cane-sugars and syrups is optically inactive, but the statement seems to have been disproved by Meissl. Besides, in raw beet-sugars and syrups, raffinose, a very strong dextro-rotatory sugar, is found vitiating the readings for cane-sugar. The correction of the original polarization in such cases is most generally made by the method of inversion proposed by Clerget. The direct polarization is taken in the usual way, and a part of the solution remaining from the one hundred cubic centimetres prepared for this test is put into a 50-cubic-centimetre flask, which has also a 55-cubic-centimetre mark on the neck. Fifty cubic centimetres having been taken, five cubic centimetres of concentrated hydrochloric acid is added, and the whole heated on a water-bath to 70° C. for some This suffices to completely invert the cane-sugar present, ten minutes. while the original invert sugar is unacted on. The flask is then cooled. and part of the liquid is filled into a 220-millimetre tube, closed by glass plates at both ends and provided with a tubulure in the side so that a thermometer may hang suspended in the liquid when the observation is The reading will generally be much reduced from the original dextro-rotatory reading, and may even be some degrees to the left. If, then, S represent the sum or difference of polariscope readings before and after inversion (difference if both are to the right, sum if the second reading is to the left), T the temperature of the inverted solution when polarized, and R the correct percentage sought,  $R = \frac{200 \text{ S}}{285 - T}$ . Clerget has also prepared an elaborate set of tables which make the use of the formula unnecessary. (See also under molasses, p. 178.)

(B) Chemical Methods.—The only chemical method for the determination of cane-sugar ever resorted to is the inversion of the cane-sugar, neutralizing with sodium carbonate, and determination of the reducing sugar so obtained by the method to be described under the next head. The inversion takes place in definite proportions, so that nineteen parts of sucrose produce twenty parts of the invert sugar. When invert sugar is also present in the solution of which the cane-sugar is to be determined by inversion, the former is first estimated as a separate operation, and then a portion of the original solution is inverted, and the total invert sugar, including that formed from the cane-sugar, is determined.

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2. Determination of Glucose, or Invert Sugar.—The oldest method is that based on Trommer's reaction as applied to sugar analysis by Barreswill and Fehling. This depends upon the fact that an alkaline solution of copper oxide containing a fixed organic acid, as tartaric, is reduced with the separation out of insoluble cuprous oxide by dextrose, or invert sugar, while cane-sugar has no effect. The composition of a standard Fehling's solution, as it is called, is thus given,\* 34,639 grammes crystallized copper sulphate are dissolved in water and brought to 500 cubic centimetres; 173 grammes Rochelle salt and 50 grammes sodium hydroxide are also dissolved in water and brought to

<sup>\*</sup> Bulletin No. 107, Bureau of Chemistry, U. S. Dept. of Agriculture.

500 cubic centimetres. Equal volumes of these solutions are mixe when required for use and constitute the correct Fehling's solution. ready-prepared Fehling's solution changes in the course of some da in effective power even when kept in a cool place and in the dark. To cubic centimetres of the Fehling's solution given above correspond .05 gramme dextrose, or invert sugar, or .0475 gramme cane-sugar mai active by inversion. For technical determinations merely the work wi the solution can be volumetric; for more exact scientific purposes it mu be gravimetric, weighing the copper as metal or as cupric oxide. carrying out the volumetric test, the sugar solution in which glucose to be determined is placed in a burette. If dark, it may be previous cleared with a small quantity of bone-black, or if it be some of the sol tion prepared for polarization, it is prepared without lead solution, a aliquot portion taken out for this glucose determination, and the r mainder treated with a measured quantity of the lead solution, for which allowance is made. Any lead in this glucose solution must be eliminate thoroughly. This is best done with sulphurous acid, the change strength in the liquid being noted. Ten cubic centimetres of the mixe Fehling's solution are now measured into a porcelain dish, diluted wi twenty or thirty cubic centimetres of water and brought quickly to bo ing, when the sugar solution is run in two cubic centimetres at a tim boiling between each addition. When the blue color has nearly disa peared the sugar solution should be added, in small amount but st rapidly. The end of the reaction is reached when a few drops of the supernatant liquid filtered into a mixture of acetic acid and dilute pota sium ferrocyanide give no brown color.

In carrying out the gravimetric method the Fehling's solution r mains in excess, while the precipitated cuprous oxide is carefully filtered off and further treated. The procedure is as follows: Sixty cubic cenmetres of the mixed Fehling's solution and thirty cubic centimetres water are boiled up in a beaker glass, twenty-five cubic centimetres the dextrose solution of approximately one per cent. strength added, as the mixture again boiled. It is then filtered with the aid of a filter-pun upon a Soxhlet filter (asbestos layer in a tared funnel of narrow cylind shape), quickly washed with hot water, and then with alcohol and ethe and dried. The asbestos filter, with the cuprous oxide, is now heat with a small flame, while a current of hydrogen is passed into the funnso that the precipitate is reduced to metallic copper. It is allowed cool in the current of hydrogen, placed for a few minutes over sulphur acid, and then weighed. A table has been constructed by Allihn which gives in milligrammes the dextrose corresponding to the weight of copp found.

Other methods for the determination of dextrose are those of Defre who determines the copper as cupric oxide (Leach, Food Inspection, ; ed., p. 593); of Munson and Walker, who weigh the copper as cupro oxide (*Ibid.*, p. 598); and of Soldaini, who uses a solution of basic cabonate of copper dissolved in potassium bicarbonate. This last reage has been recently strongly commended as better than Fehling's solutio

in that it is more sensitive to glucose and is much less affected by canesugar even after prolonged boiling.\*\*

3. Analysis of Commercial Raw Sugars.—Raw sugars contain, besides the cane-sugar, invert sugar, moisture, mineral salts, organic nonsugar, and insoluble matter. Raw beet-sugars contain, in addition to the sucrose and glucose just mentioned, small quantities of raffinose, a variety of sugar found in the beet juice and present in all the products from it.

The cane-sugar present is partly crystallized and partly uncrystallizable. Both are, of course, counted together in the polarization figures, but only the first is capable of extraction in the refining process. The method of estimating the crystallized cane-sugar for itself will be described later on. The polarization methods have already been described. In raw sugars containing much invert sugar, such as those from the cane, the double polarization (before and after inversion) is alone to be relied upon.

The methods for glucose have also been described.

The determination of moisture is made by taking five grammes of the sample and drying it spread out on a weighed watch-crystal in an airbath not over 100° C. until it ceases to lose weight. As sugars containing much glucose cannot stand the heat without some alteration, in their case a lower temperature (about 70° C.) is used. For very syrupy sugars and melados it becomes necessary to dry with the addition of a weighed amount of clean sand. Drying in a vacuum is also practised in many cases, as the operation is shortened and less risk of alteration exists.

The mineral salts are determined as ash. The following analyses give the average composition of raw cane- and beet-sugar ash according to Monier:

(	Cane-sugar.	Beet-sugar.
Potassium (and sodium) carbonate	16.5	82.2
Calcium carbonate	49.0	6.7
Potassium (and sodium) sulphate	16.0	
Sodium chloride	9.0	
		11.1
Silica and alumina	9.5	None.
	100.0	100.0

Owing to this decided difference it is much easier to get the ash of cane-sugars completely burned and in weighable condition than that of beet-sugars, which contain so much of the deliquescent and alkaline carbonates. To obviate this difficulty, Scheibler proposes to treat the sugar with sulphuric acid before igniting it, by which means the ash obtained contains the bases as non-volatile, difficultly fusible and non-deliquescent sulphates instead of as carbonates. A deduction of one-tenth of the weight of the sulphated ash must be made in this case for the increase due to the sulphuric acid. The soluble and insoluble ash are often distinguished in addition to total ash. In ordinary commercial analyses of

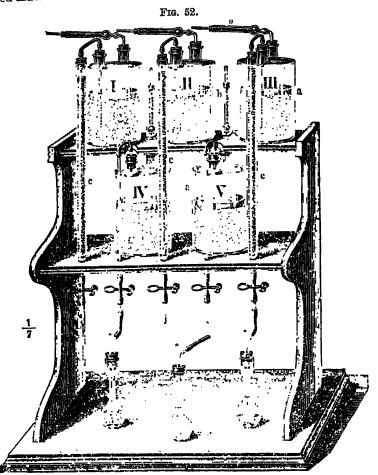
<sup>\*</sup> Bodenbender und Scheller, Zeitschrift für Rübenzucker, 1887, p. 138.

sugars, the sum of the cane-sugar, glucose, ash, and water is subtracted from one hundred, and the difference called organic or undetermined matters. This would include both the soluble organic impurities and the insoluble impurities, such as fibre and particles of cane. Two processes have been proposed for determining the soluble organic impurities separately: Walkoff's method of precipitation with tannin, and the basic acetate of lead method. Neither method is in very general use.

As before stated, the full analysis of a raw sugar will not give any exact measure of its refining value,—that is, of the amount of crystallized cane-sugar that can be extracted from it. The so-called method of coefficients adopted in France, whereby five times the ash, plus once or twice the glucose percentage subtracted from the cane-sugar percentage. is taken to represent the crystallized cane-sugar obtainable, is not much to be depended upon. The true refining value, or rendement, of a raw sugar can, however, be determined by a special procedure first proposed by Payen and afterwards improved by Scheibler. The process depends upon the fact that if raw sugars be treated with a saturated alcoholic solution of cane-sugar acidified with acetic acid, the coloring matter and other impurities, together with the syrup and other uncrystallizable constituents, are removed, while the crystallized sugar remains unchanged. The sugary alcoholic liquids are then displaced by absolute alcohol. Fig. 52 shows the arrangement of vessels. The bottle I contains eighty-five per cent. alcohol, to which fifty cubic centimetres of acetic acid is added per litre, and the mixture allowed to stand in contact with an excess of powdered white sugar for a day, being shaken at intervals; bottle II, alcohol of ninety-two per cent. saturated as the other, but without acetic acid; bottle III, alcohol of ninety-six per cent., also saturated with sugar; and bottle IV, a mixture of two-thirds absolute alcohol and one-third ether. Of the sugars to be examined, weights are taken corresponding to the polariscope used, placed in the upright tubes, washed with the successive solutions, and dried by the aid of a filter-pump ready for use in the polariscope test. In carrying out the process, the alcohol and ether mixture is first run in that it may take up any moisture and throw out the sugar that such moisture may have dissolved, then successively down to No. I, which is the effective washing solution. This is then displaced by Nos. II, III, and IV in succession. The method is thoroughly reliable, but great care must be taken to keep the alcoholic solutions just saturated with sugar through all changes of temperature.

4. Analyses of Molasses and Syrups.—The composition of both the cane-sugar and the beet-sugar molasses have already been given (see p. 169), and it was seen that they differed notably. Both still contain considerable quantities of sucrose, but for different reasons. With the cane-sugar molasses because of the invert sugar, with the beet-sugar molasses because of the melassigenic salts. In either case the polariscope reading for sucrose must be corrected by inversion. The glucose is determined as described under raw sugars. The water is determined by weighing out a sample, thinning it with water, putting it into a weighed dish with clean sand, and drying it at a temperature of 60° C.

until constant. Drying in a partial vacuum also facilitates the drying off of the moisture. The ash is determined as with raw sugars, sulphuric acid being added, and the bases weighed as sulphates instead of as carbonates, the proper correction being made. The organic non-sugar is simply taken by difference as with raw sugars. The determination of raffinose in raw beet-sugars, and particularly in beet-molasses, has attracted much attention in recent years. Creydt\* has suggested a way for



determining it in the presence of cane-sugar in connection with the method of inversion. He finds that while cane-sugar polarizing 100° to the right before inversion polarizes 32° to the left after inversion, a change of 132°, raffinose changes from 100° to 50.7° only, a change of 49.3°. He proposes two formulas: A = z + 1.57 R, and c = 1.322 + 1.57 R  $\times$  .493, in which A is the direct polarization, c the polarization after inversion, z the percentage of cane-sugar, and R that of raffinose.

<sup>\*</sup> Zeitschrift für Rübenzucker, vol. xxxvii, p. 163.

From these formulas, A and c being known, z and R can be found. The reading after inversion must be taken uniformly at 20° C.

5. Analyses of Sugar-canes and Sugar-beets and Raw Juices THEREFROM.—The very different physical characters of the sugar-cane and the sugar-beet, the one a bamboo-like shell enclosing a woody pith, and the other a soft root easily brought into pulpy consistency, make the work upon them quite different. In the case of the cane, the samples to be analyzed are weighed and then pressed between rolls, moistened with hot water and again pressed, and this repeated several times. The exhausted stalk, or "bagasse," is usually not further examined, but in the juice the sucrose, glucose, ash, and organic non-sugar are determined as before described. In all analyses of raw cane juices the percentage of total solids is determined by the Brix saccharometer or "spindle." The form of hydrometer in most general use is known as the Balling or Brix, and its readings indicate directly the percentage of impure sugar or solid matter dissolved. Sets of tables also allow of the conversion of the Brix scale into direct specific gravity figures. (See Appendix, p. 570.) With the aid of the specific gravity determination it is possible to make a rapid analysis of raw juice without weighing. The method adopted by Crampton,\* one of the chemists of the United States Bureau of Agriculture, for this analysis is to measure out a certain volume of the juice, add lead solution, make up to another definite volume, polarize, and apply the correction for specific gravity to the reading obtained. A set of tables for this correction and the factor needed in the glucose determination are given by Crampton.

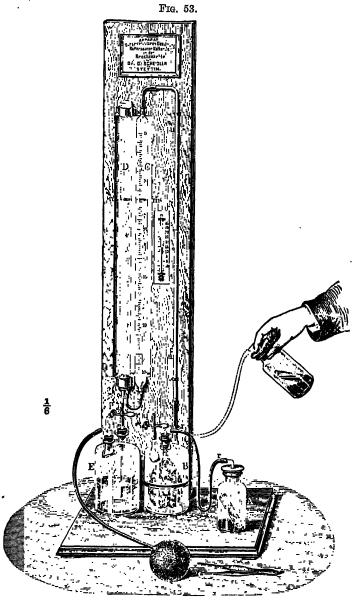
In the examination of sugar-beets, the system of pressing and moistening with hot water can be followed for the extraction of the juice, but the method proposed by Scheibler of extracting the sugar from a weighed quantity of the pulp by the aid of alcohol is much better. This is accomplished by the aid of a Soxhlet or other extractor (see p. 86) connected with an upright condenser. After complete extraction and cooling the necessary amount of lead solution is added, and the liquid brought up to the mark with absolute alcohol and then polarized. Degener has described a still simpler form of extraction, originally suggested by Rapp, in which the pulp remains in the alcoholic solution until after it is cleared with the lead solution and brought to the mark, when it is filtered and polarized. A correction must in this case be applied to the reading on account of the volume occupied by the pulp in the measured liquid.

The amount of dry residue, or "marc," of the beet can be determined in the Scheibler extraction method at the same time by taking the exhausted residue, drying it in a current of air, and weighing it. The moisture and ash of the beet are determined as with raw sugars. The organic non-sugar is gotten by difference or by one of the methods mentioned under raw sugars.

6. Analyses of Side-products.—(a) Of Bone-Black.—Careful anal-

<sup>\*</sup> United States Bureau of Agriculture, Bulletin No. 15, pp. 31-35.

vses of both fresh char and that which is in use are needed to allow of the proper control in filtration. The most important determinations are those of water, carbonate of lime, carbon, and specific gravity, as upon the changes in these depend in the main its efficiency. The water is determined by drying for several hours at 140° C. The sample should not be powdered. The carbon is determined by treating a weighed quantity of the char with pure hydrochloric acid, with the aid of heat, on a water-bath until the soluble portions have been dissolved, diluting and filtering upon a weighed quantitative filter. After thorough washing with hot water, the filter and contents are dried at 100°, placed between watch-glasses and weighed, again heated and weighed as long any loss of weight is shown. The filter and carbon are then transferred to a weighed crucible and ignited. The insoluble residue, taken from the previous weight, minus the weight of the filter, gives the amount of car-The estimation of carbonate of lime in case the char is used with cane-sugar or juices is of much less importance than when the char is used with beet-sugars or juices. In the former case, the percentage decreases at first, and then remains nearly stationary, in the repeated use of the char, while in the latter case it would increase steadily, because of the more thorough liming and carbonatation to which the beet juices are subjected, were it not for the treatment with hydrochloric acid in the revivifying of the char. (See p. 165.) To allow of the proper judgment in this use of hydrochloric acid, it becomes necessary in beet-sugar working to determine carefully the amount of carbonate of lime taken up by the char in using before starting the revivification. It is almost universally done at present by the aid of the Scheibler apparatus, shown in Fig. 53. The normal quantity of pulverized char (1.702 grammes) is placed in A, and the tube S filled with acid to the mark is carefully placed in the bottle. E is then filled with water, and the operator, by means of the compression-bulb, forces the liquid into D and C, which connect at the base, until it reaches a little above the zero-point in C. when it is allowed to flow out by opening the pinchcock at p until the level in C is at zero. The stopper now being placed in A, a connection with B is made by the tube r. If the level of the liquid in D and Cbe then unequal, the equality may be restored by opening the cock q for a few seconds, and which for the rest of the operation remains closed. The vessel A is now held, as shown in the cut, so that the acid may come in contact with the char, and the bottle gently shaken to cause the acid to mix thoroughly with the assay. The pressure of the gas evolved distends the rubber bag in B and depresses the column of water in C. The stopcock p is now opened to allow the water in D to flow out sufficiently rapidly to keep the level in C and D as near the same as possible during the progress of the determination. When all the gas has been given off and the level of the liquid in C becomes stationary, p is closed, after bringing the water in D to the same level as that in C, and the volume and temperature read off. A set of tables accompanying the instrument gives the percentage of carbonate of lime from the volume and temperature readings. Assuming seven per cent. to be the normal amount of carbonate of lime in the char, any excess, as shown in this determination, can have its equivalent in hydrochloric acid of known strength calculated, and thus the acid treatment in the revivifying process can be made accurate.



In determining specific gravity, both apparent and real specific gravity (the latter after boiling the char with distilled water to displace air) are to be taken.

(b) Of Scums, Press-cakes, and Sucrates.—In the case of the scums and press-cakes obtained in the manufacture of raw sugars, their chief value is in the lime salts they contain, which, notably in the case of beet-sugars, adapt them for use as fertilizing materials. They, however, contain such amounts of sugar, either mechanically held, or, where the carbonatation process has been used, as sucrates, as make it necessary to determine regularly the sucrose in them. In the case of the thin scums from cane-sugar working, the determination can be made exactly as with an impure juice before described. In the case of the heavier press-cake from beet-sugar working, resulting from carbonatation, the procedure is different. Here the sucrate of lime is to be decomposed if possible without decomposing the large amount of accompanying carbonate of lime. This is done by careful addition of acetic acid, controlling the reaction with phenol-phthalein. For details of this process, first proposed by Sidersky, see Frühling and Schultz, "Anleitung zür Zucker Untersuchungen," 3d ed., p. 171.

Sucrates, resulting from the working of molasses for sugar by either of the lime or strontium processes (see p. 162), are analyzed by a somewhat similar procedure, using strong acetic acid to set the sugar free from its combination with the lime or strontia and phenol-phthaleïn as an indicator. The excess of acid is afterwards neutralized, lead solution added, the solution brought to strength, and polarized. (Ibid., p. 155.)

## V. Bibliography and Statistics.

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### STATISTICS.

1. SUGAR PRODUCTION OF THE UNITED STATES.—The U. S. Census 1910 gives the production as well as importations of sugar for 1909 compared with the figures for the three previous decades:

### A. SUGAR FROM CANE IN 1909.

Louisiana	 325,500 short tons.
Texas	 8,600 short tons.

334,100 short tons.

### B. SUGAR FROM BEETS IN 1909.

	Granulated sugar (tons).	Raw sugar (tons).	Molasses (gallons).
California	. 126,600	200	2,135,800
Colorado	. 147,000	1,600	7,669,200
Michigan	. 103,900	600	5,016,700
Wisconsin	. 13,000		832,400
All other States	. 106,300	2,500	5,158,700
Total	. 496,800	4,900	20,812,800

#### C. COMPARISON OF PRODUCTION AND IMPORTS.

				Imports (in tons).		
	Produ Cane.	action (in to Beet.	ons). Total.	Non- contiguous U. S.	Other countries.	Total.
1909	 334,100	501,700	835,800	927,800	1,959,300	2,887,100
1899	 161,300	81,700	243,000	313,400	1,695,600	2,009,000
1889	 150,600	2,500	153,100	280,600	1,186,400	1,467,000
1879	 89,400	1,400	90,800	139,200	775,400	914,610

2. Production, Importation, and Consumption for the United States in 1910.—The Bureau of Statistics reports for the year ending June 30, 1910, as follows:

	1910 (tons).	1909 (tons).
Production of sugar from cane (in tons)	362,500	414,500
Production of sugar from beet (in tons)	512,500	483,500
Total production in United States	887,500	898,500
Hawaii	555,500	511,500
Porto Rico	284,500	244,000
Philippines	88,000	42,000
Total from U. S. dependencies	928,000	797,500
Total from U.S. and dependencies	1,815,500	1,695,500
Importation from Cuba	1,755,000	
Importation from Dutch Indies	157,500	
Total imports	1,959,000	2,053,800
Consumption for 1910, 7550 million pounds = 82 por		

## 3. SUGAR-BEETS WORKED AND BEET-SUGAR PRODUCED IN EUROPE.

	Sugar-beets v	worked (tons). 1909-10.	Beet-sugar pr 1910–11.	oduced (tons). 1909-10.
Germany	15,275,380	12,904,795	2,424,840	2,027,272
Austria-Hungary	9,981,400	8,166,100	1,529,800	1,245,608
France	5,383,000	6,246,850	703,330	803,006
Belgium	1,932,000	1,777,600	271,800	248,403
Holland	1,523,000	1,330,000	221,400	194,822
Russia	13,080,400	6,837,498	2,085,200	1,123,594
Sweden	1,088,300	897,000	167,160	127,000
Denmark	750,000	500,000	105,000	65,000
Italy	1,500,000	970,000	170,000	118,900
Spain	490,000	667,000	60,000	83,000
Rumania	275,000	208,000	35,000	30,775
Servia	75,000	66,000	10,000	8,630
Bulgaria	35,000	20,000	4,200	2,435
Switzerland	25,000	25,000	3,500	3,500
	51,413,480	40,415,843	7,791,330	6,081,945

### CHAPTER V.

THE INDUSTRIES OF STARCH AND ITS ALTERATION PRODUCTS.

### I. Raw Materials.

STARCH is one of the most important, as well as most widely occuring, productions of the vegetable kingdom. It constitutes, either whe extracted from vegetable raw materials, or more generally in admixtu with the other plant constituents, the staple article of food for the grebulk of the human race. It is only necessary to call attention to the fathat the principal cereal grains used throughout the world for food cotain starch as their chief ingredient, and that the tubers of many plan and the stems and roots of some trees also yield starch in great abundance

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The most complete enumeration and classification of starches is the of Muter as amplified by Allen\* and Blyth,† by which they are divide into five groups on the basis of their physical and microscopical differences, as follows:

I. The potato group includes such oval or ovate starches as give play of colors when examined by polarized light and a selenite plate ar having the hilum and concentric rings clearly visible. It includes to les mois, or canna arrow-root, potato starch, maranta, or St. Vince arrow-root, Natal arrow-root, and curcuma arrow-root.

II. The leguminous starches comprise such round or oval starches give little or no color with polarized light, have concentric rings all be invisible, though becoming apparent in many cases on treating the start with chromic acid, while the hilum is well marked and cracked, or stalate. It includes the starches of the bean, pea, and lentil.

III. The wheat group comprises those round or oval starches having both hilum and concentric rings invisible in the majority of granules, includes the starches of wheat, barley, rye, chestnut, and acorn, and variety of starches from medicinal plants, such as jalap, rhubar senega, etc.

IV. The sago group comprises those starches of which all the graules are truncated at one end. It includes sago, tapioca, and arm together with the starch from belladonna, colchicum, scammony, pod phyllum, canella, aconite, cassia, and cinnamon.

V. The rice group. In this group all the starches are angular polygonal in form. It includes oats, rice, buckwheat, maize, dari, peppe as well as ipecacuanha.

In addition to the differences in form and marking mentioned abov

<sup>\*</sup> Com. Org. Anal., 2d ed., vol. i, p. 335. † Blyth, Foods, Compos. and Anal., p. 139.

the starch-granules differ in size according to their different sources, so that under the microscope they can be distinguished by the measurement of the average diameter of the granule. This ranges, according to Karmarsch, from .01 to .815 millimetre, or from .0004 to .0079 inch.

For practical purposes we may now speak of two classes only of these starch-containing materials,—vix., the cereals and the plants in which the starch is extracted from tubers, roots, or stems, such as potatoes on the one hand, and the West Indian starch preparations, like arrow-root, sago, and tapioca, on the other. As before stated, starch is the chief ingredient in the cereals, but not at all the only one. The composition of the more important cereals is thus given by Bell:\*

Constituents.	Wheat. Winter sown.	Wheat. Spring sown.	Long- eared barley.	English oats.	Maize.	Rye.	Carolina rice (without husk).
Fat Starch Starch Sugar (as sucrose) Albumen (insoluble in alcohol) Nitrogenous matter (soluble in alcohol) Cellulose Mineral matter Moisture Total .	1.48	1.56	1.08	5.14	3.58	1.43	0.19
	63.71	65.86	63.51	49.78	64.66	61.87	77.66
	2.57	2.24	1.34	2.86	1.94	4.30	0.88
	10.70	7.19	8.18	10.62	9.67	9.78	7.94
	4.83	4.40	8.28	4.05	4.60	5.09	1.40
	3.03	2.93	7.28	18.53	1.86	8.23	Traces,
	1.60	1.74	2.32	2.66	1.35	1.85	0.28
	12.08	14.08	13.06	11.86	12.34	12.45	12.15

The chemical formula of starch is  $(C_0H_{10}O_5)_n$ . According to Tollens, confirmed by Mylius, it is  $C_{24}H_{40}O_{20}$ ; according to Brown soluble starch is  $C_{120}H_{200}O_{100}$ , while for the ordinary variety he proposes  $C_{180}H_{300}O_{150}$ . Nägeli stated that by subjecting the starch-granules to the slow action of saliva, salt solutions, and dilute acids two substances could be shown to be present, granulose, which dissolved, and cellulose (or, as it has been called, farinose), which remained. Arthur Meyer considers that there is only a single substance originally present, and that the cellulose, or farinose, which remains is a decomposition product of the starch.

Air-dried starch always retains from eighteen to twenty per cent. of water. It is soluble in cold water, alcohol, ether, ethereal and fatty oils. When it is heated with twelve to fifteen times its bulk of water to 55° C., it begins to show signs of change, swelling up, and at a temperature of from 70° to 80° C. (or even below 70° C. with some pure starches) the granules burst and it becomes a uniform translucent mass, known as "starch-paste," which is not, however, a solution, as the water can be frozen out of it. Boiled with water for a long time it goes into solution, one part dissolving in fifty parts of water. The action of heat upon starch is to change it gradually into dextrine, which is soluble in cold water.

One of the best known of the reactions of starch is the formation of a blue color with iodine. This has been carefully studied by L. W. Andrews (Jour. Amer. Chem. Society, 1902, p. 865), who considers it

<sup>\*</sup>Bell, The Analysis and Adulteration of Foods, Part ii, p. 86.

to be a dissociable addition compound of iodine with starch molecules. He finds that clear starch solutions made at a temperature of about 150° take up in the cold an amount of iodine corresponding to the formula  $(C_0H_{10}O_5)_{12}I$ , while starch heated with excess of iodine to 100° for a short time takes up an amount of iodine corresponding to the formula  $(C_0H_{10}O_5)_{12}I_2$ . The blue coloration is constantly availed of to note the presence or gradual disappearance or alteration of starch in many technical processes.

The action of dilute acids upon starch brings about the change known as "hydrolysis," and there is produced dextrine,  $C_{12}H_{20}O_{10}$ , and dextrose,  $C_{6}H_{12}O_{0}$ , the latter eventually as sole product. Many ferments, like saliva, the pancreatic ferment, and especially the diastase of malt, produce in starch a somewhat similar change and yield maltose,  $C_{12}H_{22}O_{11}$ , and a number of intermediate products between this and starch. A great deal of investigation has been devoted to these intermediate products, and as yet no absolute agreement has been reached on the subject. The following is the series of products obtained in this hydrolysis of starch as stated by Tollens:\*

Other chemists notably increase the list of these intermediate products. The existence of erythrodextrine as a distinct compound is doubted by some investigators, who consider it to be merely a mixture of achroöor maltodextrine with a little soluble starch, such a mixture giving a violet reaction with iodine. By over-treatment with acids unfermentable carbohydrates, of a character differing from any of the products named, appear to form. The name gallisin has been given to a compound of this kind, and the formula  $C_{12}H_{24}O_{10}$  ascribed to it. For a description of the conditions of its formation see later (p. 197).

Strong nitric acid in the cold acts upon starch, producing nitro derivatives, such as mono-, di-, and tetra-nitro starch, analogous to the nitrocelluloses. Alkalies and alkaline earths form combinations with starch, the barium and calcium compounds being insoluble, of which advantage is taken in the Asboth method for determination of starch. (See p. 199.)

### II. Processes of Manufacture.

1. Extraction and Purifying of the Starch.—Of the various starch-containing materials before enumerated, only a limited number are actually utilized for the extraction of the starch in a pure condition,—

<sup>\*</sup> Tollens, Kohlenhydrate, Breslau, 1888, p. 177.

viz., maize, wheat, rice, potatoes, and arrow-root. In the United States by far the greater amount is obtained from maize, or Indian corn, a limited amount only being extracted from wheat. In Europe, on the Continent, potatoes serve as the chief starch-producing material, some also being extracted from wheat and some from rice, while in the West Indies arrow-root starch is manufactured at St. Vincent and elsewhere.

In the manufacture of corn starch, after winnowing or cleansing the corn by powerful fans, it is placed in large wooden steeping-vats, holding several thousand bushels of corn, and is covered with warm water at about 140° F., to which is frequently added sulphur dioxide, making a solution of 1° B. sulphurous acid. After twelve hours this water is run off and the germ is separated after a crushing of the softened corn. While the germ is afterwards worked for the corn oil contained, the starchy portion is ground again and passes on to the separator tables, where it is continuously washed. These separator tables are inclined sieves of silk bolting-cloth, which are kept in constant motion and are sprayed with jets of water. The starch passes through the bolting-cloth with water as a milky fluid, while the coarser cellular tissue, or husk, of the corn is left behind. This residue is pressed to remove water, and sold as cattle food. The water from the shakers holding the starch in suspension is run into wooden vats, where the starch settles, and the water is drawn off and discarded. The starch is next thoroughly agitated with fresh water, to which a caustic soda solution of 7° to 8° Baumé has been added, until the milky liquid has changed to a greenish-yellow color. The object in adding the alkali is to dissolve and remove the gluten and other albuminoids, oil, etc. After sufficient agitation and treatment with alkali, the separated starch and glutinous matter is allowed to deposit, the supernatant solution of gluten, oil, etc., is allowed to run to waste, and the impure starch washed and agitated with water. It is allowed to stand at rest for fifteen to twenty minutes to permit insoluble gluten to subside, when the top one of a series of plugs arranged in the side of the vat is withdrawn, and the starch suspended in water allowed to flow by means of a gutter into subsiding-vats placed below: then the next lower plug is drawn, and so on until the last plug has been drawn. The plugs are replaced and the vats again filled with water, and the operation repeated as before. This operation, called the siphoning process, is generally repeated three times, and the three runnings of starch are collected in three separate vats, forming the three grades of starch of the factory. These three grades of factory starch are again agitated with water, sieved through bolting-cloth, and run finally as purified starch into wooden "settlers." After it has been compacted sufficiently, which is effected in boxes with perforated bottoms, it is cut into blocks and dried upon an absorbent support of plaster of Paris while heated in a current of warm air. In drying out thoroughly, any remaining impurities come to the surface with the escaping moisture and form a yellowish crust. When this is removed, the interior is found to be perfectly white. The results on a bushel of fifty-six pounds of co: are thus stated by Archbold:\*

Starch recovered	28.000	pounds.
Dry refuse for cattle food	13.700	- "
Bran (in cleansing process)	0.728	"
Moisture of the corn	5,626	"
Loss (albuminoids, oil, etc.)	7.946	"
	56,000	"

Besides this very complete treatment known as the "alkali process much of the cheaper grade of starch is purified by the use of sulphuro acid alone without the use of any alkali, and this product is known "acid process" starch.

In either case the removal of the germ as a preliminary step is no practised, as from this is obtained the valuable maize oil together wi oil cake and ground husk for cattle food. The starch is moreover o tained in a higher state of purity and the process considerably shortene lessening the danger of fermentation or souring while being treated.

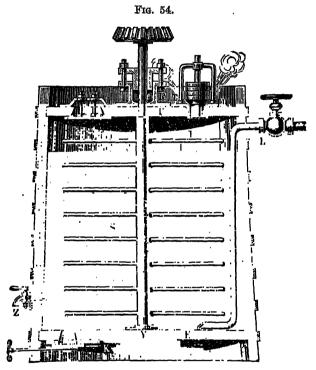
In manufacturing starch from wheat two quite different process are followed, according as the gluten is to be obtained as a side-produ or not. In the process generally known as the "sour," or fermentation process, the gluten is wasted. In this process the wheat is steeped tanks until thoroughly softened, then crushed in roller-mills, and place for fermentation in large oaken cisterns. The temperature is here mai tained at about 20° C., and the operation lasts some fourteen days, t mass being well stirred during its continuance. The sugar of the whe and a part of the starch are converted into glucose, which undergo alcoholic fermentation, and passes by oxidation into the acetous ferme tation also, acetic, propionic, and lactic acids being formed. rapidly attack and dissolve the gluten, liberating the starch-granule The impure liquor is drawn off from the starch mass, and the latter washed, either in hempen sacks while being trodden under foot or drums with perforated sides. After repeated washings and settlings ar renewed sieving through fine hair sieves the starch is sufficiently purifie Wheat starch is also obtained from wheat flour without ferme tation by what is known as Martin's process, in which a stiff doug is made of the flour. This is then washed in a fine sieve under a jet water till all the starch has escaped as a milky fluid. This leaves the gluten, of which about twenty-five per cent, of the weight of the flor is gotten suitable for use in the manufacture of macaroni, or to be use instead of albumen or casein in calico-printing.

In the manufacture of potato starch, the potatoes are washed ar then pulped by a grating or rasping machine. The grated mass, mainto a paste with water, then goes at once into the sieving machine, whe it is rubbed by revolving brushes against the wire or hair sides of t

<sup>\*</sup> Journ. Soc. Chem. Ind., 1887, p. 82.

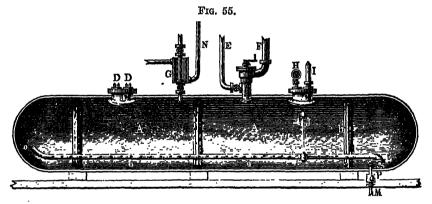
rotating cylinder, while a current of water is continuously washing out the fine starch from the pulp. The sifted and washed starch deposits in large tanks, where it is repeatedly washed by agitation and settling with fresh waters. It is then spread out on absorbent slabs to dry, or dried in drying chambers or kilns heated by steam coils.

2. Manufacture of Glucose, or Grape-sugar.—As stated on a preceding page, the action of dilute acids converts starch into dextrine, maltose, and dextrose, the last of which becomes by continued action the sole product. As it is also the most important product of this action of acids, we shall take it up first. The purified starch obtained as described in the preceding section, while yet moist, is taken for the treatment with



acids. The "conversion" can be accomplished in either open or closed converters, although the former have been practically entirely superseded by the pressure or closed converters. These converters are large, upright vessels of iron or copper lined with sheet lead to prevent the action of the dilute acids. Sulphuric acid is generally employed in the conversion if a solid grape-sugar is to be made, or hydrochloric acid preferably when glucose syrup is the product to be manufactured. Both oxalic acid and hydrofluoric acid have been used in France as the agents for the conversion. The quantity of the acid employed varies with the object of the manufacturer. For the production of "glucose," a liquid product which contains much dextrine, a smaller quantity is used than when solid "grape-sugar" is to be produced, in which the conversion into dextrose

is much more complete. The proportion varies from one-half pound oil of vitriol to one and a quarter pounds per hundred pounds of starch. When the open converter is used, a few inches of water is introduced and the acid added, or half the acid may be added to the starch mixture. The acid water is brought to a boil, and the starch, previously mixed with water to a gravity of from 18° to 21° Baumé, is slowly pumped in, keeping the liquid constantly boiling. When all the starch has been introduced, the whole is boiled until the iodine test ceases to give a blue color and shows a dark cherry color. The boiling is usually continued for about four hours. The closed converters may be made from strong wooden vats or may be of copper; they are provided with safety-valves, and are made of sufficient strength to stand a pressure of six atmospheres. Fig. 54 shows the form first introduced in this country by T. A. Hoffmann, while Fig. 55 shows the form proposed by Maubré in London. In this case the starch is mixed with water to a gravity of from 11° to



16° Baumé. This with the acid is introduced into the converter, and the whole is heated under a pressure of from forty-five to seventy-five pounds per square inch. The time required for the conversion is much shorter than in the open converters. The use of open and closed converters successively is often resorted to. The starch and water of a gravity of 15° or 16° Baumé is first boiled in the open converter for from one to two hours, then transferred to the closed converter and boiled under a pressure of from forty-five to seventy-five pounds per square inch. The time of this boiling varies from ten minutes to half an hour.

When the starch has been sufficiently converted, according to the product desired, the liquor is run into the neutralizing-vats. Here a sufficient quantity of marble-dust is added to completely neutralize the sulphuric acid (or when hydrochloric acid has been used, a solution of caustic soda). A little fine bone-black is generally added at the same time. The liquor having a gravity of 12° to 18° Baumé, and known as "light liquor," is next filtered through bag filters of cotton cloth or filter-presses. In many establishments the liquor is now treated with sulphurous acid gas to prevent fermentation, and probably to some extent

to act as a bleaching agent. It is then filtered through bone-black, by which it is decolorized and at the same time freed from various soluble impurities. Concentration is then effected in the vacuum-pan at a temperature of about 140° F. until it has a gravity of from 28° to 30° Baumé, when it is called "heavy liquor." A second bag or filter-press filtration is now resorted to in many factories to remove the sulphate of lime, which separates out at this degree of concentration. It is then filtered a second time through bone-black to secure complete decolorization and purification. The final concentration is effected by boiling the liquor in the vacuum-pan until it reaches 40° to 42° Baumé. product in which the conversion has been least complete remains liquid. and is called "glucose" in the trade; that which is ready to solidify is known as "grape-sugar." Dr. Arno Behr has patented a process for obtaining the solid grape-sugar in pure crystals. While it is still liquid there is added to it a small quantity of crystallized anhydrous dextrose. The mixture is filled into moulds, and in about three days it is found to be a solid mass of crystals of anhydrous dextrose. The blocks are then placed in a centrifugal machine to throw out the still liquid syrup. and the anhydrous dextrose remains as a crystalline mass.

3. Manufacture of Levulose.—From invert sugar (mixture of equal molecules of dextrose and levulose) levulose is now obtained as a commercial product by taking advantage of the insolubility of its calcium compound. According to Schering's patent inverted molasses is used, which has been inverted with the aid of hydrochloric acid. After the inversion is completed the solution is diluted to one-sixth strength with water, cooled to 0° C., and the levulose precipitated as the insoluble calcium levulosate. The precipitate is separated, washed with ice water, drained or centrifugated thoroughly and decomposed at a temperature not exceeding 50° with carbon dioxide under pressure. By centrifugating the lime precipitate, a syrup of thirty per cent. levulose strength is obtained. This is then acidified with a weak acid and further concentrated.

This manufactured levulose is used extensively in the manufacture of confectionery, as it prevents the crystallizing of the cane-sugar used and so prevents the gradual change of clear transparent sugar products to the opaque condition. It is also used in the manufacture of marmalades, jellies, and sugared fruits, for the treatment of wines, particularly sweet wines and champagnes. It is also used in medicine in the case of diabetes, where ordinary sugar is forbidden to be used in sweetening foods, and as the basis of infant foods.

4. Manufacture of Maltose.—By the action of the diastase of malt upon starch is formed mainly maltose. Dilute sulphuric acid will convert this by prolonged boiling into dextrose, but diastase alone will not so convert it. The manufacture of maltose on a large scale as a preparation for use in beer-brewing to simplify the preparation of a suitable wort has been attempted by several. Dubrunfaut and Cuisinier patented a process in 1883 for preparing maltose, either as syrup or crystallized, by the following procedure: One part of green or partially dried malt

is warmed with two to three parts of water, digested for several hours at 30° C., and afterwards filter-pressed to obtain an "infusion" of malt. One part of starch-flour is then suspended in two to twelve parts of water, and five to ten per cent. of infusion added, the whole gradually warmed to 80° C., then heated under a pressure of one and a half atmospheres for thirty minutes, quickly cooled to 48° C., and treated with five to twenty per cent. of infusion and hydrochloric acid (from six to twentyfive cubic centimetres of acid per one hundred litres). After one hour the mass is filtered through filter-paper fastened upon linen cloth. The solution is allowed to stand at 48° C. for twelve to fifteen hours, then concentrated to 28° B., filtered, again concentrated to 38° B., filtered through animal charcoal, and allowed to crystallize. A sample of the syrup made from corn-starch by the Brussels Maltose Company working under this patent was analyzed by Märcker,\* and found to contain 19.8 per cent. water, 78.7 per cent. maltose, 1.5 per cent. non-sugar, and no dextrine. The process is, however, said to have failed as yet of commercial success. Saare, who has recently investigated it, shows that the complete conversion into maltose only takes place with weak mashes, and he concludes from his results that the process is not suitable for German distilleries under the present conditions. O'Sullivan and Valentin! have also patented a process for producing from starch, or starchyielding substances, preferably from rice, a compound solid body, which the inventors term "dextrine-maltose," consisting of the same proportional quantities of dextrine and maltose as are ordinarily obtained from malt by a properly-conducted mashing process, and which it is intended should replace a portion of the malt used in brewing. For details, see original article. Perfectly pure maltose can be obtained by Herzfeld's process of repeatedly extracting with alcohol from the syrupy product of the action of malt upon starch. The alcohol precipitates the dextrine, but dissolves the maltose, which can then be obtained in crystalline condition.

5. SOLUBLE STARCH.—In recent years considerable attention has been given to preparing products that will either gelatinize in the cold and yield solutions with cementitious value or dissolve completely in hot water. The starch under the influence of acids, alkalies or of different oxidizing agents will be changed in substance without the starch granules losing their outward appearance.

Soluble starch is widely utilized as a substitute for dextrin, casein, gelatin, gums and glue, and specially as a basis of sizing preparations.

One of the earlier methods was to heat starch dried at 80°-90° with glacial acetic acid. The product of this treatment can be washed with cold water without loss and is soluble in boiling water without gelatinizing.

Volatile organic acids, like formic and acetic acids, are advantageously used, as they can be distilled off after the reaction and no neu-

<sup>\*</sup>Jahresber. der Chem. Tech., 1886, p. 613.

<sup>†</sup> Dingler, Polytech. Journ., 266, p. 418.

<sup>‡</sup> Journ. Soc. Chem. Ind., 1888, p. 446.

tralization of the acid is required. One per cent. of such acid acting for five to six hours at 115° C. suffices to effect the change.

Starch so prepared with acid is uniformly soluble in hot water, while soluble starch prepared with alkalies gelatinizes with cold water. To avoid the production of the alkali salts remaining in the product, ammonia has been used. The starch is treated with water containing two per cent. of ammonia and the product is dried in thin layers to volatilize the ammonia. The soluble starch so obtained forms a voluminous powder gelatinizing with cold water.

Chlorine, persulphates, and perborates have also been used.

6. Manufacture of Dextrine.—This may be effected by acting upon starch with heat alone, by the action of dilute acids and heat, or by the action of diastase. The first and second of these methods are followed in preparing the solid product. In the manufacture by heat alone the limits of temperature are 212° to 250° C., although Payen says that 200° to 210° C. produces the most perfectly soluble dextrine. The starch is heated in revolving drums, which are frequently double-jacketed, and contain oil in the outer space in order to insure uniform heating. After the moisture is given off, the loss of weight in roasting is small, two hundred and twenty pounds of starch giving one hundred and seventy-six pounds of finished dextrine.

In the manufacture by the aid of acids the starch is mixed with dilute nitric or hydrochloric acid so as to form a damp powder. This is exposed to a temperature of 100° to 120° C. until the transformation is complete, which can be determined by applying the iodine test from time to time. The process must be arrested promptly when the starch is all changed, or the dextrine will pass rapidly into glucose. Oxalic acid is also sometimes employed in the manufacture of dextrine.

7. MANUFACTURE OF SUGAR-COLORING (Caramel, or Zucker-couleur).— Very considerable quantities of an artificial coloring material for use in coloring beer, rum, cognac, and high wines are made on the Continent of Europe from starch. For the manufacture of rum and cognac coloring. starch is treated with dilute sulphuric acid, as before described for the manufacture of dextrose and dextrine mixtures, but the heating is continued until all the dextrine has been changed into dextrose, as determined by taking a sample from time to time and testing it with an excess of ninety-six per cent. alcohol. When no longer any turbidity from separated dextrine shows, the reaction is considered as finished. sulphuric acid is then neutralized with carbonate of lime, and after sufficient standing the clear liquor is run off from the precipitated sulphate of lime. It is now concentrated to 36° B. and filtered. The hot filtrate is then run into a vessel provided with mechanical agitation and heated to boiling, when crystallized soda salt (three kilos. of soda to one hundred kilos. of sugar solution) is added in small portions at The contents of the kettle froth and must be continuously stirred. White and inflammable vapors are given off and the color rapidly deepens. The heat is now gradually lessened to prevent carbonizing of the contents of the vessel, and the color is tested. A drop chilled by heing dropped into water should harden and be brittle and

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should taste bitter. The contents of the kettle are then cooled some what by adding hot water. When the production of the color is completed, the contents of the kettle are extracted with water, filtered to remove carbonized particles, and then tested as to quality. The coloring is made in several grades or depths of color, which are also differently soluble, the one in seventy-five per cent. alcohol and the other in eight per cent. alcohol. For beer- or wine-coloring it is not necessary to be a careful to use a glucose freed perfectly from dextrine, and, instead a soda, ammonium carbonate is taken. The product is soluble in water but not so readily in alcohol.

### III. Products.

1. STARCH.—The properties and action of reagents upon starch have already been noted in speaking of it as a raw material. It is only nece sary to subjoin a few analyses of commercial starches in order to sho the character of that usually obtainable. Those of potato and whe starch are by J. Wolff, as quoted in "Wagner's Chemical Technology, and those of corn starch are by Dr. Archbold, as given by him in the "Journal of the Society of Chemical Industry," 1887, p. 188.

PERCENTAGE COMPOSITION.	Potato starch. (Wolff.)	Wheat starch, I. (Wolff.)	Wheat starch, II. (Wolff.)	Corn starch, I. (Archbold.)	Corn starch, II. (Archbold.)	Corn starch, III (Archbold.
Starch	88.59 0.50 0.53 15.38	88.91 0.10 1.44 0.03 14.52	79.63 1.84 3.77 0.55 14.20	98.50  0.30 1.20	92.88 } 2.88 0.60 4.14	90.88 4.25 0.65 4.77
Total	100.00	100.00	100.00	100.00	100.00	100.00

2. Glucose and Grape-sugar.—Starch-sugar appears in commer in a great variety of grades and under a similar variety of names. I already said, in the United States the name glucose is in general applic to the liquid products, while that of grape-sugar is given to the sol products. In France, where large quantities of similar products a manufactured, the liquid product is known as "sirop cristal" and the solid product "glucose massé." The following analyses show the corposition of the commercial products as now manufactured by the Corproducts Co.\*

	Corn syrup.	70 sugar.	80 sugar.	Anhydrot sugar.
Water	per cent. 19.0 38.5 42.0 0.5	per cent. 19.7 70.2 9.3 0.8	per cent. 11.2 79.9 8.0 0.9	94.6 0.7 0.7

<sup>\*</sup> Journ. Soc. Chem. Ind., 1909, p. 347.

- 3. Maltose.—Maltose forms fine white crystalline needles aggregating in warty groups, which have a faint sweetish taste. It is soluble in water and methyl and ethyl alcohol, but more difficultly in the last than dextrose. Its formula is C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>, and it crystallizes with one molecule of water, which it loses slowly at 100° C. in a vacuum. Its specific rotatory power is, according to Meissl,  $(S)_d = 140.375 - .01837 P - .095 T$ . where P equals the percentage strength of the solution and T the temperature. A ten per cent. solution at 20° C. would then be 138.3°. O'Sullivan takes it as 139.2° for a ten per cent. solution. Its reducing power with Fehling's solution is frequently stated to be two-thirds that of dextrose, but Brown and Heron as well as O'Sullivan make it more exactly sixty-two per cent. of that shown by dextrose. It has no action. however, upon Barfoed's reagent (see p. 200), which is reduced by dextrose. Maltose is said to be directly and completely fermentable without previous change into dextrose, but more slowly than this latter, so that if a mixture of maltose and dextrose be fermented with yeast, the whole of the dextrose disappears before the former sugar is acted upon.
- 4. Dextrine.—Pure dextrine is a white amorphous solid. It is tasteless, odorless, and non-volatile. It is completely soluble in cold water, but the commercial varieties usually leave from twelve to twenty per cent. or even more of starch and other insoluble residue when dissolved. Heated with dilute acids it yields maltose and ultimately dextrose. It is unfermentable if free from sugar. It has no reducing power on Fehling's solution. Probably what is called dextrine is a mixture of products obtained in the breaking down of the complex starch-molecules. Some investigators claim to have obtained sixteen distinct modifications or varieties of dextrine in this way. We have before (see p. 187) alluded to amylodextrine, erythrodextrine, achroödextrine, and maltodextrine.

Commercial dextrine, or "British guin," gives a brown coloration with iodine, and probably consists largely of erythrodextrine. The following analyses by R. Forster give an idea of the composition of the dextrines usually obtainable:

PERCENTAGE COMPOSITION.	First quality dextrose.	Dark- burned starch.	Brown dextrine.	Gommel- ine.	Old dextrine.	Light- burned starch.
Dextrine	72.45 8.77 13.14 5.64	70.43 1.92 19.97 7.68	63.60 7.67 14.51 14.22	59.71 5.76 20.64 13.89	49.78 1.42 30.80 18.00	5.34 0.24 86.47 7.95
	100.00	100.00	100.00	100.00	100.00	100.00

Dextrine is used as a substitute for natural gums, especially for gum arabic. It is thus used in calico-printing and in the mordanting and printing of colors upon most other classes of textile goods, for mucilage, for glazing cards and paper, as warp-dressing, and in the manufacture of beer. It forms the crust on bread by the change of the starch of the flour in baking, and is present in most products from starch or starch-sugar.

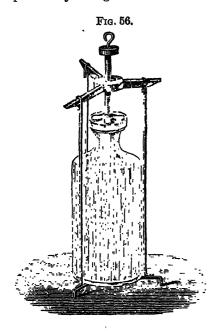
5. UNFERMENTABLE CARBOHYDRATES (Gallisin).—The presence of a unfermentable carbohydrate in starch-sugar was long since pointed o by O'Sullivan. The compound which has been specially studied is know as gallisin, and is prepared by fermenting a twenty per cent. solution starch-sugar with yeast at 18° or 20° C. for five or six days. resultant liquid was filtered, evaporated to a syrup at 100° C., and shake with a large excess of absolute alcohol. The treatment with alcohol w repeated several times until the unaltered sugar and other impuriti were removed, the syrup being converted into a yellowish crumblis mess, which, by pounding in a mortar with a mixture of equal parts alcohol and ether, was obtained as a gray powder. After purifying wi animal charcoal and drying over sulphuric acid, the gallisin was obtainas a white amorphous extremely hygroscopic powder. Its taste is at fir sweet, but afterwards becomes insipid. It is easily decomposable by her even at 100° C. It is readily soluble in water, nearly insoluble in abs lute alcohol, and but slighly more soluble in methy alcohol, in whi respect it differs from dextrose. Gallisin is stated to have the compotion C<sub>12</sub>H<sub>24</sub>O<sub>10</sub>. Its concentrated aqueous solution is distinctly acid litmus and a sparingly soluble barium compound may be obtained then from by adding alcoholic baryta. It reduces nitrate of silver on heatin especially on addition of ammonia, reduces bichromate and perma ganate, and precipitates hot Fehling's solution. Its cupric oxide redu ing power (dextrose = 100) is stated to be 45.6°. Gallisin is dextr rotatory, the value for  $S_d$  being stated to be 80.1° in twenty-seven p cent., 82.3° in ten per cent., and 84.9° in 1.6 per cent. solutions. I heating with dilute sulphuric acid for some hours gallisin yields a lar proportion of dextrose, but its complete conversion has not so far beeffected.

It is doubtful whether "gallisin" as hitherto obtained is really definite compound, but the possibility of isolating a reducing or optical active body from the liquid left after fermenting solutions of many specemens of sugar-starch cannot be ignored in considering the composition of commercial glucose.

## IV. Analytical Tests and Methods.

1. For Starch.—The usual method for the determination of stars is to invert by the action of dilute acid, and then determine the dextroproduced by the aid of Fehling's solution. In this case one hundre parts of dextrose are taken as indicating ninety of starch. It has be found, however, that the change to dextrose by the aid of dilute sulphur acid is not complete, that other non-reducing bodies are formed, at that but ninety-five per cent. of the starch is converted into dextrose The hydrolysis is more completely effected by the aid of hydrochlor acid, as carried out in Sachsse's method. 2.5 to 3 grammes of dry star (or so much of the starch-containing substance as would correspond this amount of starch) are placed in a flask with two hundred cult centimetres of water and twenty cubic centimetres of hydrochloric ac

and heated on the water-bath with inverted condenser for three hours. (Märcker states that heating for three hours with this amount of hydrochloric acid does not give more than ninety-six to ninety-seven per cent. of the starch as sugar, as some of the latter is destroyed. He recommends using fifteen cubic centimetres of acid and heating for two hours.) The contents of the flask are then nearly neutralized with sodium hydroxide, filled to the mark, and the dextrose determined by Fehling's solution. If other carbohydrates or cellulose are present, which would be also converted into dextrose by hydrochloric acid, the starch must be previously brought into the soluble form, which may be done by heating



with water to 130° C. in a pressureflask like that of Lintner, shown in Fig. 56. Or the starch may be hydrolyzed in part by infusion of malt or diastase at 62.5° C., filtered from cellulose, etc., and then treated with hydrochloric acid for complete hydrolysis as above. In this latter case, the process of Reinke\* is the simplest. Three grammes of the sample as finely powdered as possible are heated to boiling with fifty cubic centimetres of water, cooled at 62.5° C., and hydrolyzed for an hour at this temperature with .05 gramme of diastase. This is prepared according to Lintner's procedure, by making an alcoholic twenty per cent. extract (1:3) of raw malt, adding to the filtrate two volumes of ninety-six per cent. alcohol, separation of the precipitated

diastase, washing with alcohol and ether, and drying in a desiceator. The mixture is then cooled, diluted with water to two hundred and fifty cubic centimetres, and filtered. Of the filtrate, two hundred cubic centimetres are taken and hydrolyzed, as before described, with fifteen cubic centimetres of hydrochloric acid of 1.125 specific gravity for two and a half hours, when the solution is neutralized and the dextrose determined.

A more elaborate course of treatment, following in the main the same lines as the procedure of Reinke just described, but stopping with the action of the diastase, has been published by O'Sullivan, and is given at length by Allen.† In this case the filtered liquid, assumed to contain nothing but maltose and dextrine, is made up to one hundred cubic centimetres, and the density determined. It is then tested with Fehling's solution for the maltose, and the dextrine deduced from the rotatory power of the solution. The maltose found, divided by 1.055, gives the

<sup>\*</sup> Jahresber. Chem. Technol., 1887, p. 863.

<sup>†</sup> Commercial Organic Analysis, 3d ed., vol. i, p. 415.

corresponding weight of starch, which, added to the dextrine found, gives the total number of grammes of starch represented by one hundred cubic centimetres of the solution.

The method for the determination of starch in cereals most generally used in Germany at present is that of Märcker.\* Three grammes of substance are placed in a small beaker (preferably of metal), which is placed as one of several in a Soxhlet pressure-boiler, or the test is carried out in the Lintner pressure-flask, figured on the preceding page, and heated to the temperature of boiling water. It is then cooled to 60° to 65° C., five cubic centimetres of thin malt infusion are added, and it is digested at this temperature for some twenty minutes. It is then made faintly acid (one cubic centimetre of tartaric acid suffices) and heated under a pressure of three to four atmospheres. It is then cooled down and an additional five cubic centimetres of malt infusion added, with which it is digested an half-hour. The solution is then brought up to one hundred cubic centimetres, filtered, and determined with Fehling's solution, either by titration or by weighing the reduced copper.

Of other methods proposed for starch determinations it is only necessary to notice the Asboth method, proposed in 1887. It depends on the fact that starch forms a compound with baryta-water,  $C_{24}H_{40}O_{20}BaO$ , containing 19.1 per cent. of BaO, which is insoluble in forty-five per cent. alcohol. The baryta-water is used in excess, and the free alkaline earth determined by titration with decinormal hydrochloric acid. Numerous experimenters have taken exception to the method that the results were variable, and that starch combined with varying amounts of barium oxide. To these objections the author made a reply later,† and claims that the presence of fat in the cereals interferes with the accuracy of the determination, and that if the fat be previously extracted by ether, the determinations in the fat-free residue are accurate and concordant. J. Napier Spence, in the "Journal of the Society of Chemical Industry," for 1888, p. 77, has also come to the defence of the Asboth method and shown the conditions under which it yields accurate results.

- 2. Glucose, or Dextrose.—For the determination of dextrose alone the Fehling's solution affords the most accurate means. For its use, see analysis of raw sugars, p. 174. In the absence of any other optically active body its examination with the polariscope will also suffice. For mixtures like commercial glucose, which contains dextrose, maltose, and dextrine, see later.
- 3. Maltose.—This variety of sugar, as before stated, has optical activity and reducing power on Fehling's solution. It can, however, be distinguished from dextrose by its failure to reduce Barfoed's solution, which is reduced by dextrose and invert sugar. This reagent is made by dissolving one part of neutral copper acetate in fifteen parts of water, to two hundred cubic centimetres of which five cubic centimetres of thirty-eight per cent. acetic acid is added. Boiled for several minutes with maltose solution it shows no reduction.

<sup>\*</sup> Jahresber. Chem. Technol., 1885, p. 863.

<sup>+</sup> Chemiker Zeitung, 1889, pp. 591 and 611.

- 4. Dextrine.—Pure dextrine differs from dextrose and maltose in showing no reducing power with either Fehling's solution or with Knapp's mercuric cyanide solution. It can, indeed, be freed from admixture with dextrose and maltose by heating with an excess of an alkaline solution of mercuric cyanide, which oxidizes these two varieties of sugar, leaving the dextrine unaffected. (See Wiley's method below.)
- 5. Commercial Glucose and Similar Mixtures derived from Starch.—As commercial glucose is likely to be a mixture of the three compounds, dextrose, maltose, and dextrine, its analysis and the determination of the several constituents becomes a frequently-recurring problem. Three methods have been proposed. The first, by Allen,\* requires the determination of moisture and ash in the sample, which, subtracted from 100, leaves the total organic solids, O. The apparent specific rotatory power, S, and the cupric oxide reducing power (in terms of dextrose reduction = 100), K, are now determined. Then, if m be the maltose, g the dextrose-glucose, and d the dextrine, Allen determines the respective percentages by the use of the formulas  $m = \left(S \frac{52.7 \ K + 198 \ (O K)}{100}\right) \div .313$ ,  $g = K .62 \ m$ , and d = O (g + m)

The author states that the presence of gallisin or other unfermentable sugar may vitiate the values of K and S, as observed, and so make the results inaccurate.

The second method is that of Wiley,† which is based upon the theory that boiling with an alkaline solution of mercuric cyanide will destroy the optical activity of maltose and dextrose, leaving that of dextrine unchanged. The cupric oxide reducing power of the sample is ascertained in the usual way by Fehling's solution. The specific rotatory power is determined by polarizing a ten per cent. solution (previously heated to boiling) in the ordinary manner. Ten cubic centimetres of this solution used for polarizing are then treated with an excess of an alkaline solution of mercuric cyanide, and the mixture boiled for two to three minutes. It is then cooled and slightly acidulated with hydrochloric acid, which destroys the reddish-brown color possessed by the alkaline liquid. The solution is then diluted to fifty cubic centimetres, and the rotation observed in a tube four decimetres in length. The angular rotation observed will be due simply to the dextrine, the percentage of which may then be calculated by the formula

rotation  $\times$  1000  $\times$  cubic centimetres of solution polarized = per-198  $\times$  length of tube in centimetres  $\times$  weight of the sample taken centage of dextrine. The percentages of dextrose and maltose may be deduced from the reducing power of the sample, or from the difference in specific rotatory power before (S) and after (s) the treatment with alkaline mercuric eyanide. Thus,  $K = 1.00 \ g + .62 \ m$ ,  $S = .527 \ g + 139.2 \ m + 1.98 \ d$  and  $s = 1.98 \ d$ , whence  $m = \frac{S - s - .527 \ K}{1.06526}$ . g can now be

found from the first of the three equations, and then d in the second.

<sup>\*</sup> Commercial Organic Analysis, 3d ed., vol. i, p. 365. † Chemical News, xlvi, p. 175.

Wiley's process was employed by the Committee of the National Academy of Science in their investigation of commercial glucose from corn starch. It is, however, based upon several assumptions that have not been specifically proven, and especially in the presence of any considerable quantity of maltose are its results open to doubt. (See Allen, "Commercial Organic Analysis," 3d ed., vol. i, p. 369, foot-note.)

The third method of estimating the constituents in commercial glucose is due to C. Graham, and is probably more exact than either of those before mentioned. Dissolve five grammes of the sample in a small quantity of hot water and add the solution drop by drop to one litre of nearly absolute alcohol. Dextrine is precipitated, and on standing becomes attached to the sides of the beaker, while maltose, gallisin, and dextrose are soluble in the large quantity of alcohol employed. If the solution be then decanted from the precipitate, the dextrine in the latter can be ascertained by drying and weighing, or by dissolving it in a definite quantity of water and observing the solution, density, and rotation. The alcohol is distilled off from the solution of the sugars and the residual liquid divided into aliquot portions, in one of which the gallisin may be determined after fermentation with yeast, while others are employed for the observation of the specific rotation and reducing power, which data give the means of calculating the propertions of maltose and dextrose in the sample.

1879.—Die Stürkefabrikation, F. Stohmann, Berlin.

1881.—Starch, Glucose, and Dextrine, Frünkel and Hutter, Philadelphia.

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1884.—Report on Glucose by the National Academy of Sciences, Washington.

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1888.-Handbuch der Kohlenhydrate, B. Tollens, Breslau.

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V. Bibliography and Statistics.

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#### STATISTICS.

1. Production of Starch in the United States and Germany.—
O. Saare in 1896 gave the following summary of the production in these chief producing countries:

	United States. Hundred kilos.	Germany. Hundred kilos.
Potato starch	120,000 180,000	2,000,000 3,000,000
Corn starch	2,000,000 3,000,000	25,000 — 50,000
Wheat starch	150,000 — 200,000	50,000 — 100,000
Rice starch		200,000 — 250,000
	2,270,000 - 3,380,000	2,275,000 — 3,400,000

2. PRODUCTION OF GRAPE-SUGAR (STARCH-SUGAR), GLUCOSE, DEXTRINE, ETC.—The same authority gives the following figures for the products from starch:

Sugar-color (caramel)	United States. Hundred kilos.	Germany. Hundred kilos.		
Grape-sugar and glucose syrup	2,500,000 — 3,000,000	350,000 400,000		
Sugar-color (caramel)		30,000 40,000		
Dextrine	20,000 — 50,000	150,000 — 180,000		
	2,520,000 — 3,050,000	530,000 620,000		

3. Production of Starch in the United States (Census of 1905):

	1900.	1905.
Corn starch produced (lbs.)	247,051,744	150,520,009
Value	\$6,133,001	\$4,702,309
Potato starch produced (lbs.)	33,941,826	27,709,400
Value	\$1,129,129	\$924,476
Cassava and wheat starch (lbs.)	16,809,569	17,845,121
Value	\$775,835	\$1,124,612
Total starch (lbs.)	297,803,139	196,074,530
Value	\$8,037,965	\$6,751,397

4. Corn Products.—The corn crop of the United States in 1908 is said to have been 2,643,000,000 bushels, valued at \$1,615,000,000. Of this, ninety per cent. is used as food and ten per cent. is used in the industries and for export.

Two per cent., or 50,000,000 bushels, is used in the starch and glucose industry.

Four per cent., or 100,000,000 bushels, is used in the fermentation and milling industry.

Four per cent., or 100,000,000 bushels, is exported.

(T. B. Wagner, Jour. Soc. Chem. Ind., 1909, p. 343.)

5. Exportations of Starch, Glucose, and Grape-sugar from the United States.

	1908.	1909.	1910.
Starch (lbs.)	48,125,851	33,228,278	51,535,570
Value	\$1,042,054	\$780,155	\$1,274,773
Glucose (lbs.)	98,608,192	92,652,409	112,730,639
Value	\$1,898,652	\$1,138,406	\$2,623,131
Grape-sugar (lbs.)	31,078,642	19,572,095	37,098,449
Value		\$407,683	\$792,089
(Commerce	and Navigation	of the United S	tates, 1910.)

### CHAPTER VI.

#### FERMENTATION INDUSTRIES.

### A. NATURE AND VARIETIES OF FERMENTATION.

UNDER the term fermentation are included certain methods of decomposition of organic compounds which presuppose the presence of definite substances called "ferments," which do not, however, apparently take part in the chemical reactions but act after the manner of the inorganic catalytic agents. Their presence in relatively small amount and the existence of conditions of temperature, etc., favorable to them, suffice to bring about the decomposition of large quantities of the fermentable material.

The ferments which seem to determine the decomposition may be either soluble unorganized ferments or insoluble organized ferments, which are minute vegetable growths. The decompositions which are brought about by organized ferments differ quite notably in their results from those which can be induced by mere chemical reagents. Thus, the decomposition of sugar into alcohol and carbon dioxide, as it is brought about by the activity of the yeast-cell, cannot be brought about by purely chemical treatment. On the other hand, the action of the unorganized ferments is much more analogous to that induced by chemical reagents. Thus, the hydrolytic action of diastase on starch can also be perfectly imitated by treating with dilute acids. Buchner has, however, recently shown that the liquid expressed from fresh yeast cells after triturating them can produce all the changes attributed to the cells themselves, and that it owes its activity to an enzyme called zymase, which is produced by the cells.

With regard to the chemical nature of the enzymes, or soluble ferments, we only know that they belong to the class of proteids. A recent analysis of diastase by Lintner may be taken as typical of the class: carbon, 46.66 per cent.; hydrogen, 7.35 per cent.; nitrogen, 10.42 per cent.; sulphur, 1.12 per cent.; and oxygen, 34.45 per cent.

While soluble in water and glycerol they are insoluble in alcohol, and are precipitated from aqueous solutions on addition of lead acetate. Their activity is destroyed by heating, that of diastase at 75° C., and all by boiling with water. Their activity is not destroyed by the presence of antiseptics, which arrest the action of the organized ferments. Thus, chloroform, thymol, and salicylic acid will all arrest the activity of the organized growth but not interfere with that of the soluble ferments. Sodium fluoride in one per cent. solution is said to check entirely the growth of the organized ferments, but is without action on those which are soluble.

Foremost among the soluble ferments is diastase. This is the ferment formed from the albuminoids of the cereals during the process of germination. It is especially developed in the malting process as applied to barley. Its chief function is the saccharification of the starch of the grain, changing it into dextrine, maltose, and dextrose.

The amount of starch that a given quantity of diastase can convert cannot be stated with absolute certainty, as it varies with the conditions of its preparation, the strength of the infusion, and other points. Its progress can, of course, be controlled by the iodine reaction, as stated under starch. Commercial extracts of malt are infusions of malted barley, which contains the products of the inversion of the starch. The solid extracts obtained by evaporation of these infusions in vacuo at low temperatures should be readily soluble, and should show that they still contain active diastatic ferment by being able to convert their own weight of starch within a short time.

Invertase.—Invertase is capable of converting cane sugar or sucrose into invert sugar. This rather resistant enzyme may be readily extracted from the yeast by various means. From yeast cells which have been killed with chloroform it may be extracted with water, and is precipitated from a water solution by the addition of alcohol. This white precipitate is readily dissolved in water and possesses the property of inverting cane sugar or sucrose quantitatively. Invertase is an important enzyme in the fermentation of molasses or any other substance containing sucrose. Invertase acts only in a slightly acid solution. The best temperature for its action is about 55° C.; it is slowly destroyed at about 65° C., and immediately at 95° C.

Zymase.—This enzyme in reality forms a class by itself, in that it possesses the property of converting monosaccharid sugars into alcohol and carbon dioxide. The presence in solution of the enzyme which Buchner named zymase, and which is the cause of alcoholic fermentation, overthrows to a great extent the older theories which regarded the actual cause of the transformation of sugar into alcohol and carbon dioxide as a vital process dependent upon the actual life activities of the yeast cell itself.

The organized ferments or vegetable growths may be divided into three classes: first, mould-growths; second, yeast-plants, or the different species and varieties of Saccharomyces; and, third, bacteria, belonging to the two genera Schizomycetes and Schizophycetes. The most important fermentations from an industrial point of view are the alcoholic, which is brought about mainly\* by the presence of ferments of the second class, and the acetic and lactic, which are brought about by ferments of the third class. Upon the alcoholic fermentation depend three important groups of industries,—viz., the manufacture of malt liquors, the manufacture of wines, and the manufacture of ardent spirits, or distilled liquors. Upon the acetic fermentation depends the manufac-

<sup>\*</sup>Buchner (1897) has shown clearly that there is present in the yeast-cells, even when dead, a soluble ferment or enzyme capable of developing the alcoholic fermentation.

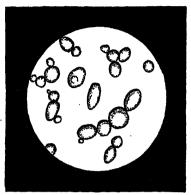
ture of different varieties of vinegar, and upon the lactic fermentation the manufacture of cheese and other milk products.

The alcoholic fermentation is always meant when we use the word fermentation in the narrower sense, as with reference to the change which starch and saccharine bodies most generally undergo. In this fermentation, the action of the yeast-plant seems to differ according to the variety of sugar presented to it. Dextrose is most immediately acted upon, the main reaction being  $C_0H_{12}O_0 = 2C_2H_0O + 2CO_2$ , although, as Pasteur first showed, side-products like glycerine and succinic acid are also formed, and in practice only about ninety-five per cent. of the dex trose is decomposed by the main reaction. Cane-sugar is not immediately fermentable. If it has been previously exposed to the action of dilute acids, it is changed into invert sugar, which then acts like dextrose. The veast-plant can effect the same change itself. Invertin (or invertase, as it is also termed) is a soluble ferment existent in yeast. It has the prop erty of rapidly and completely effecting the transformation of cane sugar into invert sugar, but is without sensible action on dextrose, levu lose, maltose, or milk-sugar. Towards dextrine its action is not se certainly negative.

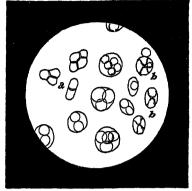
The conditions of the activity of the yeast-plant have been studied by many chemists, but notably by Pasteur. It has been found that if an abundance of air is supplied the plant grows and multiplies but fer mentation proceeds very slowly, when the supply of air is limited, the fermentation proceeds more rapidly while the growth of the cells is largely arrested, and that in the absence of air the fermentation proceed with greatest rapidity, although the plant-cells do not grow any longer but gradually disintegrate and die. Pasteur's dictum, that "fermentation is the consequence of life without air," is no longer taken as strictly accurate, as with the cessation of the growth and extension of the yeast-plant (which is dependent upon air like the life of any other plant), although its fermentation activity then becomes greatest, it begins at the same time a decay which leaves it after a time dead and inactive

The genus Saccharomyces has already been alluded to as the activ agent in the alcoholic fermentation. The species Saccharomyces cerevisi is generally known as the special beer ferment and the Saccharomyco cllipsoideus as the wine ferment. Moreover, of the Saccharomyces cer visice, two well-marked varieties have been recognized. The one is the most active at the ordinary temperature (16° to 20° C.), and carrithrough its fermentative work in from three to four days; the other works at a lower temperature (6° to 8° C.) and the fermentation is muc The first, placed in a saccharine liquid, is carried by the carbo dioxide which it liberates to the surface of the liquid, where it continu its activity; it is therefore known as a surface or top yeast. The secon on the contrary, is not carried up, and rests during its entire activion the bottom of the fermenting vessel, and is hence called a botto Two quite distinct methods of beer-brewing are practised (s p. 212), depending upon the use of the one or the other of these varieti of yeast. It has been found, however, in practice that, even when a to

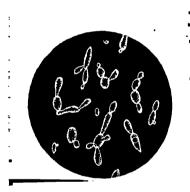
Fig. 57.



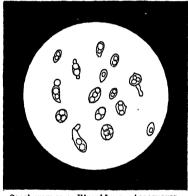
Saccharomyces cerevisiæ. (After Hansen.)



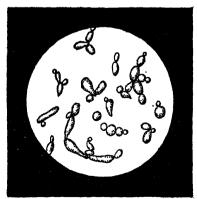
Saccharomyces cerevisiæ. Ascospores. (After Hansen.)



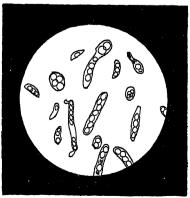
Saccharomyces ellipsoideus. (After Hansen.)



Saccharomyces ellipsoideus. Ascospores. (After Hansen.)



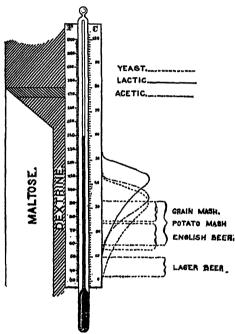
Saccharomyces Pastorianus. (After Hansen.)



Saccharomyces Pastorianus. Ascospores. (After Hansen.)

yeast is used exclusively or a bottom yeast exclusively, the results are not always uniform. These anomalies are now made clear through the researches of E. Ch. Hansen, of Copenhagen, who has applied the methods of pure cultivation introduced by bacteriologists to the study of the yeast-plant. He has found that if a single yeast-cell of one of the better varieties of Saccharomyces be cultivated with the precautions needed to exclude what is called "wild yeast" (germs present in the air, notably in the summer months), absolutely uniform results can be gotten in brewing. Beginning in 1883, he has developed the study, and it has

F1G. 58.



now been accepted by most of the leading authorities on fermentation. He first decribed six species: Saccharomyces cerevisiæ I., Saccharomyces Pastorianus I., II., and III., Saccharomyces ellipsoideus I. and II., of which the second, fourth, and sixth cause bitterness and turbidity (so-called "diseases" in beer). He has since\* increased the list of varieties of ferments studied to forty, including both top and bottom yeasts, ferments similar to yeast but not belonging to the genus Saccharomyces, and forms of mould-growh. He divides the representatives of each genus into two groups according as they secrete invertin or not.

Fresh yeast resembles a dirty yellowish-gray sediment of unpleasant odor and acid reaction, made up of an immense number of vegetable cells. Three of the pure culture varieties of yeast-plant as obtained by Hansen are shown in the illustration Fig. 57, together with the special appearance of the ascospores of the same. Of these, the Saccharomyces

<sup>\*</sup> Journ. Soc. Chem. Ind., 1889, p. 471.

cerevisiæ and Saccharomyces Pastorianus are beer ferments, while the Saccharomyces ellipsoideus is the wine ferment. For many purposes (bread-baking, use in distilleries, etc.), the ferment is prepared as compressed yeast in cakes, generally with the addition of potato starch.

The special conditions of the alcoholic fermentation are: first, an aqueous solution of sugar of the strength of one part sugar to four to ten parts water; second, the presence of a yeast ferment. If this is not added already developed and active, or if the fermentation is to be spontaneous,—that is, brought about by spores from the air,—the conditions for the development of these spores must also be present. There must be protein compounds and phosphates of the alkalies and alkalie earths. Thirdly, the temperature must remain within the limits 5° to 30° C., or, more generally, from 9° to 25° C. Above 30° C. the alcoholic fermentation readily passes into the butyric and other decomposition.

The effect of temperature upon the several different ferments is shown in the graphic illustration of Fig. 58, which represents also the influence of temperature upon the decomposition of starch by diastase. On the right side of the figure, the regularly-dotted line represents the yeast curve. A slight fermentation is already induced at a temperature very little over the melting point of ice. As the temperature rises its activity increases until the maximum is reached, at about 33° C. (92° F.), when it diminishes down to nothing again, and at 50° C. (122° F.) or thereabouts it is killed. The activity of the acetic ferment is represented at the same time by the irregularly-dotted line, and that of the lactic ferment by the uniform black line.

# B. MALT LIQUORS AND THE INDUSTRIES CONNECTED THEREWITH.

### I. Raw Materials.

1. Malt.—Malt is prepared by steeping barley or other grain in water, and allowing it to germinate in order to change the character of the albuminoids and develop the ferment diastase, which then begins to act upon the starch, the germination and change being stopped at a certain stage by heating in a kiln. The composition of the unmalted barley was given among other cereals on p. 186. The changes which it undergoes in composition by the process of malting will be seen by comparing this with the two analyses of pale malt following, which are by O'Sullivan:

	No. I.	No: II.
Starch	44.15	45.13
Other carbohydrates (of which sixty to seventy per cent. consist of		
fermentable sugar), inulin and similar bodies soluble in cold water		19.39
Cellular matter		10.09
Fat		1.96
Albuminoids soluble in water	6.71	5.31
Albuminoids insoluble in water	6.38	8.49
Ash	2.60	1.92
Water	5.83	7.47
	100.00	100.00

O'Sullivan states that malt contains no ready-formed dextrine, be that it does contain from sixteen to twenty per cent. of fermental sugars, of which about one-half is probably maltose, and due to teransformation of starch in the malting process, while the remaind exists ready formed in the barley, and is not identical with the sugproduced in the malting.

Besides the diastase, a second soluble ferment is formed during t malting process, the so-called peptase, which in the mash process chang the proteids of the malt into peptones and parapeptones, which gi

nutritive value to the beer.

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A high percentage of starch in the barley to be used for brewing desirable in order that when malted it may yield a large amount "extractive matter." According to Lintner and Aubry,\* a good may should yield at least seventy-one per cent. of extract reckoned on to weight of dry substance. This determination of the value of a samp of malt is one of the most necessary of analytical tests for the malster brewer. (See p. 219.)

Well-malted barley is always yellow or amber-colored, shading brown. On breaking the grain, the interior should be of a pure whi color and floury appearance, except when the drying has been inte tionally carried so far as to partially caramelize the sugar.

Malted wheat, corn, and rice are at times used as partial substitut for the barley malt, as well as potato starch and starch-sugar. The u of patented maltose and maltose-dextrine preparations has already be referred to. (See p. 193.)

2. Hops.—Hops are the female unfructified blossoms (catkins) of t. hop-plant (Humulus lupulus). Under the thin membranous scales the strobile or catkin is an abundance of a yellowish resinous powde consisting of minute sessile grains, to which the name lupulin has be given. The active principles of the hops, contained mainly, but n exclusively, in the lupulin, are: First, the ethereal oil, which is prese to the amount of .3 per cent. in the air-dried hops. This is yellowis of strong odor and of burning taste. It consists of a hydrocarbo C<sub>5</sub>H<sub>8</sub>, and an oxygenized oil, C<sub>10</sub>H<sub>18</sub>O<sub>2</sub>, which by atmospheric oxidation becomes valerianic acid, C<sub>5</sub>H<sub>10</sub>O<sub>2</sub>, to which old hops owe their odd Second, the lupulin also contains a resinous bitter principle, which easily soluble in alcohol, but difficultly soluble in water, and extreme bitter. This is supposed to be an oxidation product of lupulinic aci which can be gotten in white crystals, speedily becoming resinous. Bo the acid and its oxidation products seem to be held dissolved in the ethereal oil. Hops also contain tannic acid of a variety allied to more tannic acid and turning iron salts green. Analyses of two well-knov Bohemian varieties of hops are given.

The blossoms are produced in August, and the strobiles are fit f gathering from the beginning of September to the middle of Octobe according to the weather. The prompt drying of the fresh-picked ho

<sup>\*</sup> Jahresber. Chem. Tech., 1882, pp. 840 and 851. †König, Nahrungs- und Genussmittel, vol. ii, p. 409.

is necessary in order that they may be safely baled. This drying takes place by the aid of hot air in a so-called hop-kiln at a temperature of about 40° C., the hops being repeatedly turned with a light wooden shovel as they lie spread out upon a false or perforated floor. When

Percentage Composition.	Water.	Ethereal oil.	Soluble in alco- hol.	Of which is resin.	alcoh	e from ol solu- water.	Tannic acid in aqueons extracts.	Ash free from CO <sub>2</sub> .	Carbon dioxide in 100 of ash.	Sand.
From Saatz	9.90	0.13	20.12	14.57	11.24	5.42	2.52	10.01	8.71	0.91
	10.61	0.17	20.97	15.14	10.51	5.10	8.18	7.87	9.51	0.81

dry they are pressed by hydraulic presses into compact bales. Hops are also often treated with sulphurous acid gas from burning sulphur to preserve them, although this sulphuring is oftener used with old hops for the purpose of brightening them in color and improving their appearance.

A number of bitter principles have been mentioned as used at times as substitutes for hops in beer-brewing, although it is doubtful if such substitution is much practised. Among these substitutes have been noted quassia, gentian, picrotoxin, the bitter principle of *Cocculus Indicus*, colchicum, wormwood, and picric acid.

3. Water.—The water used in malting and brewing must be adapted for the purpose in order to get good results. A pure and soft water or a moderately hard calcareous water will do, but it is indispensable that the water be perfectly free from organic impurities. Continental brewers use soft waters most generally in brewing beers, while English brewers prefer gypsum waters for their ales which are specially designed to keep. This is shown in the character of the water of Burton-on-Trent, which contains notable quantities of calcium and magnesium sulphates, calcium carbonate, and sodium chloride.

### II. Processes of Manufacture.

1. Malting of the Grain.—Although malt has been described as a raw material of the brewing industry, the preparation of it from the raw grain is a process so closely connected with the success of brewing that it must be described, and especially, too, because it is often combined under the same direction as the brewing process. The process of changing barley into malt is to be divided into four stages: the steeping, the couching, the flooring, and the kiln-drying. The first three of these stages have to do with the germination or development of the acrospire, or plumule, which as it develops brings about great changes in the chemical constitution of the grain, developing from the albuminoid matter the diastase, which in turn begins to act upon the starch, forming from it maltose and dextrine. At the same time during the germination atmospheric oxidation is going on at the expense of the starch of the

grain, water and carbon dioxide being steadily given off. When the development of the diastase is supposed to have reached the right point which can only be judged of by the growth of the acrospire, or germ, the fourth stage of the process is reached, and the germ must be killed the heat, which is done in the kiln-drying.

The first process of steeping is to give the grain sufficient moisture allow germination to begin. For that purpose it is put into large iro or cemented vats. These are half filled with water and the grain adde with constant stirring. The sound grains sink shortly under the water and the dead or imperfect grains float and can be removed. The wat soon takes color and odor, and must be replaced by fresh water. The dur tion of the steeping is usually forty-eight to seventy-two hours, depen ing upon the temperature, and in winter-time or with older barley ma last considerably longer. The end of the treatment may be told by noting the character of the grain. It has swollen and become nearly sufficient soft to allow of being pierced with a needle and yet exuding no juic It has gained from forty to fifty per cent. in weight and increased fro twenty to twenty-four per cent. in bulk. To offset this gain due to wat absorption, it has lost from one to two per cent, of its substance, part carried off in the steep water and partly given off as gas. The water then run off, and after draining it is turned upon the couching-floc where it remains at first in heaps of from fifteen to twenty-four inch in depth. Here it soon begins to heat up, and a rise in temperature from 7° to 10° takes place. It also begins to "sweat," and gives off a abundance of carbon dioxide, and an agreeable cucumber-like odor recognizable. The germination is now under way and the rootlets sho The "couching" stage lasts from twenty-four to thirty-six how and during that time the grain must be turned several times. heated barley must now be spread on the floor in shallow layers so as check somewhat the rate of growth of the germ, and must be turn from four to six times a day as the growth proceeds. The depth of t layer is at the same time reduced from fifteen to four or five inche During this time the germinating grain must have an abundance air. The process lasts from seven to ten or even twelve days, accordi to the season of the year, and its termination is decided by the length the germ, which must be about two-thirds that of the grain. The le in weight during the germinating process, according to Lintner, is to per cent. of the weight of the grain. The loss comes mainly upo the starch, which has in part been changed into maltose and dextrir but has mostly been oxidized to water and to carbon dioxide. To mo efficiently remove the carbon dioxide which would interfere with t germinating process and to prevent too strong a heating, the pneumal process of malting has been proposed by Galland. In this process t steeped barley is placed on a perforated floor in thick layers, and regulated current of moist, well-cooled air is kept passing through This process is now replacing the other quite largely. Still anoth form of mechanical malting apparatus is that of Saladin.\* The gern

<sup>\*</sup> Dammer's Handbuch der Chemischen Technologie, vol. iii, p. 63%.

nation must now be stopped promptly, lest it go too far at the expense of the starch of the grain, and this is best effected by heat. The germinating grain may, however, be simply dried thoroughly in the air and the rootlets removed by mechanical means. This constitutes air-dried malt, which is used for some purposes. Most generally it is dried in a kiln at a considerably higher temperature. This must be gradually applied, as if, while the raw malt were full of moisture, it were to be heated strongly, the starch would be gelatinized and the grain made tough, hard, and glassy. It is therefore heated first to about 90° F., and this is gradually raised to 150° F., or even in some cases to 180° F. A light gradual heat produces a "pale" malt, a stronger heat "yellow" or "pale amber," and then "amber" and "brown" malt. may have two floors, on the upper and cooler of which the moist malt loses its water and then passes on to the lower and hotter floor, where it is heated to the higher limit requisite for developing its empyreumatic odor and flavor, or the heating may all be effected on a single floor, in which case more time is needed for the several stages of heating. Black malt used for coloring is heated in revolving coffee-roasters, and most of the sugar is caramelized.

2. Preparation of the Wort.—The malt after being cleansed and crushed (not ground fine) is ready for use in what is known as the mashing process. This is designed not merely to extract the maltose and dextrine of the malt, but mainly to allow the diastase of the malt to act upon the starch, changing it into maltose and dextrine and the peptase to form peptones from the proteids. It must therefore be carried out under such conditions of temperature and dilution as have been found to be most favorable for effecting these purposes. already seen (p. 207) that the action of diastase is most effective at about 62.5° C. (144.5° F.), and therefore at a temperature not much above this is the infusion most successfully made. At a temperature of over 75° C. its power is destroyed. Two quite distinct processes for mashing are at present followed: the infusion, or thin mash, and the decoction, or thick mash, process. The first is used in England and France, the second in Bayaria, Bohemia, and the principal brewing centres of the Continent. Both are used in this country. In the infusion process, water at 60° to 70° C. is run into the mash-tub, a vessel provided with false bottom and mechanical agitation, the crushed malt added and stirred in, and then additional hotter water, so that a temperature of 70° C. (158° F.) is gradually attained. This is maintained for some time with constant agitation of the liquid, so that the diastase may have time to act upon the starch. The completion of this action is determined by taking a few drops of the wort from time to time and testing with iodine solution, which finally produces no color on mixing. clear infusion is now run off from under the false bottom of the tub to the copper boilers, and the malt again covered with hot water and mashed for one-half to one hour longer at 70° C. or somewhat higher now. When this is run off, hot water at 200° F. is sprinkled upon the malt from a revolving "sparger" and allowed to drain off. The wort from this third mash is not always added to that of the first and second mashes, but is used to mash a fresh quantity of malt.

In the Bavarian thick-mash process, the malt is put in the mash-tub with some cold water, and then by the addition of boiling water is brought to 35° C. A third of the softened malt is then taken out and brought gradually to boiling with water in the copper. After one-half to three-quarters of an hour's boiling, the half of this is then returned to the mash-tub and thoroughly agitated with what remained there. The temperature of the mash-tub is thereby brought to about 50° C. A second portion of the thick mash is again taken out and boiled in the copper for three-quarters to one hour, when the greater part is returned to the mash-tub and thoroughly mixed, bringing up the temperature here to 65° C. The thinner part of the mash, or clear wort, is now run off and boiled in the copper for fifteen minutes and returned, whereby the temperature of the mash-tub is brought to 75° C. This is now left at rest for an hour to an hour and a half, and then the wort is run off to the copper. The malt is washed by the sparger, and so the saccharine liquor adhering displaced. The whole process is easily understood by reference to Fig. 59, in which A is the mash-tub and C the copper for boiling up the successive portions taken from A.

It is obvious that in the thick-mash process that portion of the diastase contained in the material which is taken out and boiled is destroyed, but the boiling thoroughly disintegrates the malt and converts its starch into a paste. When this is returned to the mash-tub, it is very rapidly acted upon by the remaining diastase, of which there is quite sufficient, and changed into maltose and dextrine. By the thick-mash process, the sugar formation is held in check and the amount of extract increased.

In the mash process the diastase acts upon the starch of the malt, changing it into maltose and dextrine. The ratio of these products to each other changes according to the temperature used in the mashing. Moreover, as dextrine is not fermented in the main fermentation and only partially in the after-fermentation, some of it remaining in the finished beer, this matter of temperature of mashing is obviously of importance for the character of the beer.

According to Märker and Schultze, at temperatures up to 65° C. the reaction takes place as follows:

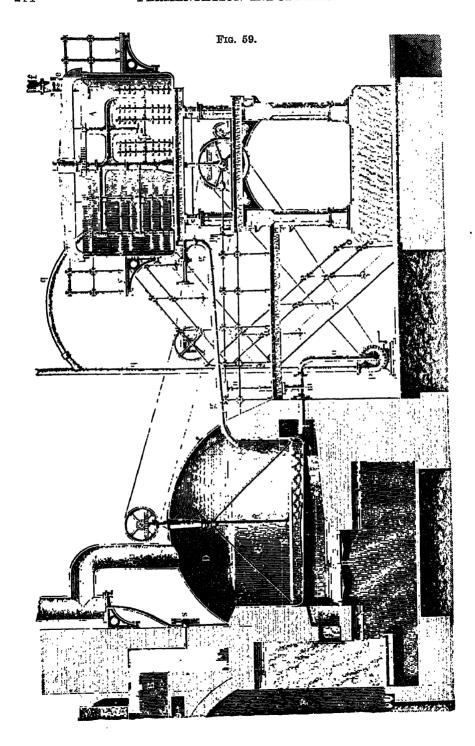
$$4C_{0}H_{10}O_{5}+2H_{2}O=C_{18}H_{34}O_{17}+C_{0}H_{10}O_{5};\\$$

that is, four molecules of starch react with two molecules of water to form three molecules of fermentable sugar (maltose) and one molecule of dextrine. On the other hand, at temperatures over 65° C. the reaction becomes—

$$6C_6H_{10}O_5 + 2H_2O = C_{18}H_{34}O_{17} + 3C_6H_{10}O_5; \\$$

that is, six molecules of starch react with two molecules of water to form one molecule of maltose and three molecules of dextrine.

The results of practice, at all events, show that in the infusion process, which takes place at low temperatures, beers of lower extract percentage are formed which is in part due to this difference in the production of dextrine just illustrated. A second drawback of the infusion



process is that it is difficult to avoid here a larger formation of lact acid, due to the more prolonged action of the water upon the malt, which is at just the temperature (about 50° C.) favorable for the formation lactic acid. At the temperature of the infusion process the nitrogenous compounds are also less completely decomposed than in the decoctic process, so that a beer obtained by the former process furnishes a monutritious ground for the growth of bacterial ferments than the latter.

As the amount of diastase in the malt is sufficiently large to sacch rify considerably more starch than that contained in the malt itsel at times unmalted grain and starch-containing cereals are added. Then to be attained is not only the saving of the cost of a portion of the malt, but to obtain a beer richer in extract and therefore of better keeping quality.

These malt substitutes are generally cereals rich in starch, such corn and rice. At times unmalted barley, rye, oats, and even potato have also been used. Care must be taken that the saccharification these cases of the use of corn and rice is made as complete as possible and hence it must not be overlooked that the starch of both corn arrice requires a higher temperature (71° C.) for its complete changing into fermentable sugar. The corn or rice before use should be shelled deprived of the germ, and crushed, so as to facilitate the liberation of i starch. The amount of malt substitute thus used should not in any call exceed thirty per cent. of the weight of the malt. In some countries, in Bavaria, the use of malt substitutes is strictly prohibited by law.

The character of the wort is to be controlled by the use of the Baling saccharometer (see p. 179), as the specific gravity of aqueous material extract corresponds to that of cane-sugar solutions of the same percentage strength.

3. Boiling and Cooling.—The wort is drained off from the mal residue, or "draff," and run into the copper boiler, where it is boile while the hops are added at once in amount varying from one to thr (or more in the case of India ales) parts to the hundred of malt, lightherest taking the least amount, lager beers next, and heavy export bee the largest amount. If the amount of hops is to be calculated after the wort has been formed, 0.25 to 0.30 kilos. may be taken to the hectolit of wort of 10 to 12 per cent., 0.40 to 0.60 kilos. to the hectolitre of wo of 12 to 15 per cent., and 0.70 to 0.80 kilos. to the hectolitre of strong worts.

The boiling accomplishes several desirable changes in the wort: first the unhydrolized protein material present separates out, which result facilitated by the action of the tannic acid of the hops, which also throw out any unchanged starch; second, the wort is concentrated; third, the valuable constituents of the hops (hop-bitter and ethereal oil) are taked up by the wort and give to the beer its taste, aroma, and keeping qualities. The time of boiling varies considerably, requiring to be longer feworts prepared by the infusion process than for those by the decoction process. From one to two hours is generally sufficient where the word on not specially need to be concentrated. Too long boiling is injurious as the volatile oil of the hops may be lost thereby. Of one hundred par

of dry malt, sixty-five to eighty per cent. are taken up as extract in the wort; of one hundred parts of hops, twenty to thirty parts.

The wort is now to be cooled preparatory to the fermentation. cooling must be effected as rapidly as possible, so that the lactic fermentation and similar changes may not take place. The cooling is generally effected in very shallow wide tanks, which are placed where a good circulation of air can be assured. From these tanks the still warm wort is often run through a circuit of pipes cooled by ice-water flowing around them, or is run in thin streams (known as a "beer fall") over a series of pipes through which cold water or chilled brine from the refrigerating apparatus circulates. Such an arrangement has now come into general use in large breweries provided with artificial refrigeration. Of course, in such a method of cooling the wort is exposed for a considerable time to impure air containing spores, which, getting into the liquid, may afterwards affect the fermentation. In all cases where Hansen's pure yeast is to be employed the wort must be cooled in vessels to which only sterilized air has access. For an arrangement of this kind, see Wagner's "Chemical Technology," 13th ed., p. 911. It is thus cooled down to the point needed for the beginning of the fermentation. This point depends upon the character of the fermentation, whether with top yeast or bottom yeast; for the latter it must be some 8° to 10° C. below that needed for the former. The cooled wort is now allowed to deposit a sediment of coagulated albuminoids, particles of hops, etc., which were suspended in it when the cooling began. This sediment is gathered and pressed and the liquid added to the rest of the wort.

4. FERMENTATION OF THE WORT.—The wort may either be left to spontaneous fermentation depending upon the spores of yeast ferments. which are always present in the air of a brewery, or it is started into fermentation by the addition of yeast. The former method is followed in Belgium, but in the great majority of cases elsewhere fermentation is incited by the direct addition of a suitable yeast. As stated before in the section on the nature of fermentation (see p. 205), there are two radically different methods of carrying out this process in practice; the surface fermentation and the bottom fermentation. The first of these, followed almost exclusively in England for all malt liquors and in this country for ales, is specially adapted for worts rich in maltose, and takes place more rapidly, at a higher temperature, and produces more alcohol. As English worts, moreover, are usually prepared by the infusion method, a considerable quantity of soluble gluten is left in the liquor, which on exposure to the air, as in half-empty casks, may start the acetic fermentation, or souring. The second of these, followed in Germany and Austria and in this country for lager-beer, proceeds more slowly; the production of alcohol is restrained by the low temperature, and as the fermentation proceeds with freer and more prolonged access of air, the yeast-plants in their growth consume the proteid matter as food. Consequently there is less albuminoid matter left to start souring, and the beer is a better-keeping beer than those prepared by the more rapid surface fermentation. Of course, the proportion of malt and hops used and the alcohol percentage also come into consideration in the

matter of keeping quality, and may offset the advantage just mentioned The fermentation, by whichever method carried out, may be divided interestages: first, the main fermentation, which begins shortly after the addition of the yeast, and is specially characterized by the decomposition of maltose, the formation of new yeast-cells, and the rise of temperature second, the after-fermentation, in which the decomposition of maltos still continues, but the formation of yeast-cells has nearly ceased, and the yeast particles suspended in the beer settle out and the beer clears and, third, the still fermentation, which follows the completed after-fermentation, in which maltose is still decomposed and some dextrine is changed into maltose by what diastase is present, but the yeast-cells are no longer formed.

The fermenting vessels are great oaken tuns holding fifty to on hundred barrels. The thick froth, or magma, of yeast is added in amour varying from one-half to three-quarters of a litre per one hundred litre of wort of ten to fourteen per cent. It may either be added direct to th whole body of the wort and stirred in, or may be mixed with a smalle amount of the wort, allowed to stand for four to five hours until fe: mentation starts, and then the mixture added to the main body of th wort. In the surface fermentation process, the main fermentation last from four to eight days, during which time the temperature must h carefully regulated and held at from 14° to 18° C. The surface is a first covered with a white foam which rises and curls and breaks int a variety of forms. The temperature rises from two to four degrees, an care must be taken to control and reduce this, which used to be done by the use of conical cans, or "swimmers," holding ice, floated at the to of the tun, cooling the mass, but the tuns are now cooled just as the fe menting cellars are, by artificial means. The fermentation is not allowe to go to completion at this initial temperature, but the beer is tran ferred for the after or slower fermentation to cooler cellars (of about 5° C.), where it is put into storage-casks. After sufficient time here, is drawn into casks containing beechwood shavings, to which isingla is sometimes added to clear it, and there is added to it some fresh fe menting beer ("Kräusen"), in the proportion of one barrel to twent which starts a new fermentation, giving the beer its "head." In the bottom fermentation, the fermenting cellar is kept at 4° to 5° C., ar the main fermentation lasts from nine to ten days. The after-ferme tation follows in cellars cooled to 1° to 2° C., and lasts corresponding

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Berlin weiss-beer is brewed from malted wheat to which some malted barley is added, and is fermented at relatively higher temperature (10 to 24° C.). At the end of the main fermentation, which is finished three days, it is transferred, with the addition of some fresh fermential beer, to tightly-stopped stone jugs, in which the after-fermentation take place. In eight to fourteen days it is in condition for drinking. It of course, effervescing, is somewhat turbid, and has a sour taste fre lactic acid which has formed.

5. Preservation of Beer.—Beer or ale intended for export may

course have keeping qualities imparted to it in its manufacture by special addition of hops, or otherwise, but most beers can have their keeping qualities improved by direct treatment after they are finished beverages. This is most legitimately done by the process of "Pasteurizing," which consists in heating the beer either already bottled or in casks to a temperature of about 60° C., which apparently kills all ferments which develop the souring of beer. Less legitimate and forbidden by law in most countries is the addition of salicylic acid, boric acid, or calcium bisulphite.

#### III. Products.

The various designations that have been given to malt liquors do not necessarily imply distinctive differences in the character of the product. They represent largely the different usages of different countries and localities. Thus, in England Ale was at one time brewed without hops, but the term now is applied to a beer brewed by the surface fermentation process, which is practically the only method used in England. Porter has now come to mean a dark malt liquor, made partly from brown or black malt, the caramel in which gives it the sweetness and syrupy appearance, and containing four or five per cent. of alcohol. Stout is a stronger porter, with larger amount of dissolved solids, and containing six or seven per cent. of alcohol.

Lager-beer is beer as brewed in Germany by the bottom fermentation process, which process is, moreover, retarded, so that the beer has better keeping qualities. It also has a larger amount of hops used in its production. It is brewed in winter for storage and use in summer. Schenkbeer is also a bottom fermentation beer, but is designed for use as soon as finished, and the process is somewhat quicker than with lager-beer, and a smaller amount of hops is used. Bock-beer is a stronger lager-beer, made with one-third more malt, and brewed specially in the spring of the year. Weiss-beer, as before stated, is made chiefly from malted wheat, and is yet in the after-fermentation. Most other names are from localities, and represent the characteristic products of those places.

The composition of various English and German beers is given in the accompanying table on the authority of Professor Charles Graham. (Allen, Commercial Organic Analysis, 2d ed., vol. ii, p. 92.)

	Maltose.	Dextrine,	Albuminoids. (Wanklynized.)	Ash, coloring, etc.	Total solids.	Acetic acid.	Lactic and succinic acid.	Alcohol.	Ratio of solids to alcohol.
Burton pale ale Burton bitter ale Mild X XXX Scotch export, bitter Dublin stout, XX Dublin stout, XXX Vienna lager Pilsen lager Munich lager	1.75 1.62 1.87 2.88 1.62 3.45 5.35 1.64 0.69 1.57	2.48 2.60 1.88 2.04 2.50 8.07 2.09 2.74 2.65 8 15	0.21 0.16 0.20 0.30 0.30 0.26 0.43 0.36 0.20	0.55 0.87 1.80 1.48 0.70 1.76 1.40 1.12 0.59 1.82	5.18 5.42 5.89 6.80 5.21 8.71 9.52 5 90 4.22 7.08	0.02 0 01 0.04 0.02 0.16 0.01 0.04 0.02 0.02	0.14 0.17 0.14 0.10 0.09 0.17 0.25 0.13 0.09 0.14	5.37 5.44 4.60 6.50 5.00 5.50 6.78 4.69 3.29 4.75	1:1.05 1:100 1:0.85 1:0.96 1:0.96 1:0.63 1:0.71 1:0.78 1:0.80

The composition of various American beers and ales as analyzed by C. A. Crampton, of the United States Department of Agriculture, is also given.\*

	Maltose.	Dextrine.	Albuminoids.	Free acids as lactic.	Ash.	Phosphoric acid.	Extract.	Alcohol.	Specific gravity.
Milwaukee lager, bottled bottled beer St. Louis export beer St. Louis pale lager, bottled St. Louis in Britanger beer bottled Reading ale, bottled Reading porter, bottled	1.10 1,06 1.82 1.75 2,14 2.17 2.51 1.46 2,14 0.59 0.93 2.67	1.57 2.68 3.04 2.87 2.51 2.75 2.58 2.30 2.57 0.90 1.99 2.88	0.51 0.40 0.406 0.556 0.463 0.675 0.538 0.531 0.531 0.731	0.057 0.057 0.071 0.074 0.067 0.067 0.046 0.086 0.086 0.282 0.382 0.166	0.196 0.809 0.224 0.846 0.812 0.812 0.183 0.241 0.265 0.401 0.472 0.412	0.065 0.056 0.057 0.077 0.074 0.064 0.093 0.078 0.095 0.095 0.077	4.18 5.40 5.88 6.26 6.15 4.64 6.82 5.22 5.94 3.46 5.55 8.19	4.28 4.42 4.16 5.06 4.40 4.28 4.68 4.29 4.52 6.24 6.92 4.89	1.0100 1.0140 1.0183 1.0187 1.0178 1.0178 1.0203 1.0147 1.0181 1.0059 1.0125 1.0269

## IV. Analytical Tests and Methods.

1. For Malt.—The brewing value of a sample of malt is dependen upon three factors,-namely, the proportion of soluble or extractive matte it will yield to water; the character of this extractive matter; and th diastatic activity. The extractive matter in malt is usually determine by a miniature mashing process. This is carried out, according to th accepted method of the Institute of Brewing in England, as follows The malt is first crushed uniformly fine; fifty grammes are then weight out as rapidly as possible (on account of its hygroscopic character), an placed in a weighed beaker with 360 cubic centimetres of distilled water previously heated to 154° to 155° F. The beaker is covered with watch-crystal and placed in a water-bath so that its contents are kept. a temperature of 150° F. for fifty-five minutes. The mash is stirred at i tervals of ten minutes during this time. The temperature is then raise to 150° F. in five minutes, and the whole mash washed into a flask gra uated to four hundred and fifteen cubic centimetres, cooled to 60° I made up to the mark at the same temperature, well shaken, and filtere through a large ribbed paper. The specific gravity of the filtrate is the determined at once at 60° F. compared with water at that temperatur For most purposes, it is sufficiently accurate to make up the unfiltered wo to four hundred and fifteen cubic centimetres, filter a portion through dry filter and take the density. The draff is here assumed to measu fifteen cubic centimetres, and the tedious washing is dispensed wit The excess of density over that of water (taken at 1000) multiplied 1 2.078 will give the percentage of dry extract yielded by the malt. Th method is based on the fact that each gramme of malt extract per hu dred cubic centimetres of infusion has been shown by experiment raise the density of the liquor by 3.85 degrees (water = 1000).

<sup>\*</sup>United States Department of Agriculture, Bulletin No. 13, Part iii, p. 282. † Allen, 4th ed., vol. i, p. 134.

figure 2.078 is then the fraction  $\frac{8}{3.85}$ . Instead of ascertaining the

gravity of the infusion, the proportion of solid matter may be determined by evaporating a known measure of the wort to dryness in a flat-bottomed dish so that the residue may form a thin film. This is dried at 105° C. and weighed. Other methods are those of Metz,\* with the use of Schultze's tables, and of Metz as improved by Weiss.

The determination of diastatic power in a sample of malt is also of importance in valuing it, even if the full diastatic power is not likely to be called out in the brewing process, where it is usually in excess of the need for the production of a beer-wort. The process of Lintner adopted by the Institute of Brewingt determines by the aid of Fehling's solution the amount of maltose produced by the action of a cold infusion of the malt upon a measured starch solution. This supposes that the action of diastase upon starch in the cold is always uniform and produces the same relative amount of maltose, which is now regarded as a matter of some uncertainty. The method proposed by Dunstan (Allen, 2d ed., vol. ii, p. 278) simply notes the end of the transformation of the starch by the absence of color with iodine solution. For it five grammes of very finely-powdered malt are digested and agitated for one hour with fifty cubic centimetres of cold water. The liquid is then strained off and the residue again digested for an hour with fifty cubic centimetres of water, and the liquids are then mixed and made up to one hundred cubic centimetres. Five-tenths gramme of starch (dried at 100° C. before weighing) is gelatinized by boiling with water, and the cold liquid diluted to one hundred cubic centimetres. The solution of malt extract is then added to twenty cubic centimetres of this mucilage by instalments of one cubic centimetre, at intervals of half an hour, until it ceases to give any color, when a small quantity is tested with a dilute solution of iodine. If less than one cubic centimetre of the solution produces this effect, more of the mucilage should be added and the operation continued.

To determine the soluble proteids of malt assumed to represent the diastase C. Graham proposes to use the Wanklyn albuminoid-ammonia process.

2. For Beer-worts.—The determination of the specific gravity of the wort is of importance, as from this may be calculated the total solid matter in the wort. If from the specific gravity of the wort we take 1000, and divide the difference by 4,‡ we get the number of grammes of solid extract contained in one hundred cubic centimetres of the wort. For the purpose of the brewer special forms of hydrometers have been constructed, the readings of which are immediately available. Thus, Bates's saccharometer gives readings of pounds per barrel (of thirty-six gallons),—that is, excess of weight in pounds of a barrel of wort over the same bulk of water. These readings can then be converted into real

<sup>\*</sup> Stohmann und Kerl, Technische Chemie, 4th ed., pp. 1345-1351.

<sup>†</sup> Allen, Com. Org. Analysis, 4th ed., i, p. 136.

<sup>†</sup> See Allen, Com. Org. Anal., 4th ed., vol. i, p. 140.

specific gravity figures by a simple proportion, using the weight of barrel of pure water, of this wort with the excess of weight shown by the saccharometer reading and the specific gravity of pure water as term. The Bates saccharometer readings can be converted into those of Ballin

or Brix by the following formula: Balling  $=\frac{260 \text{ Bates}}{360 + \text{Bates}}$ . The method of ascertaining the original gravity of beer-worts which has undergone fermentation is described later. (See following page.)

In brewing, the relative proportion of maltose and dextrine in the wort is of great importance and is liable to considerable variation, being dependent on the temperature at which the mashing was conducted, th length of time occupied in the process, and the diastatic activity of the malt employed. The composition of the wort largely influences the su sequent fermentation, as a wort containing little dextrine will produc a beer of low density which will clarify readily, but be "thin" an apparently much weaker than beer of the same original gravity by higher final attenuation. C. Graham estimates the maltose and dextrir in beer-worts from the cupric oxide reducing power of the solution before and after inversion. (For details of his procedure, see Aller vol. ii, p. 274.) West Knight (Analyst, vii, p. 211) has described very simple and rapid method of approximately determining the detrine in beer-worts. Ten cubic centimetres of the wort is treated in small weighed beaker with fifty cubic centimetres of methylated spirit ( .830 specific gravity. This causes the precipitation of the greater par of the dextrine, which after a few hours collects on the bottom of the beaker as a gummy mass, from which the alcoholic liquid can be poure off. The deposit is rinsed with a little more spirit, and the beaker drie in the water-oven and weighed. To the weight obtained an addition ( .045 gramme is made as a correction for the dextrine retained in solu tion by the spirituous liquid.

3. For Beer.—The specific gravity of the beer is a determination that is necessary as a basis of calculation for the other determination as to its composition. It should be made after freeing the beer from carbon dioxide as fully as possible. It can be made with a specific gravity flask, but is most readily and accurately carried out with Westphal specific gravity balance (see Fig. 30), which for this purpose is provided with a fourth rider giving the fourth place of decimals.

The amount of extract is frequently determined by taking a definition volume of beer of which the specific gravity has been determined, evalorating it to one-third its bulk, and then adding water sufficient to restor it to original bulk. The specific gravity of this liquid is then determine as just described. The percentage of extract can now be found by reference to Schultze's tables for determining the amount of extract the specific gravity, or more simply by O'Sullivan's method, in which the excess of this specific gravity over 1000 divided by 4 gives the number of grammes of dry extract per one hundred cubic centimetres of the beer. C. Graham considers it decidedly more accurate to evaporate five

cubic centimetres of the beer on a flat watch-crystal in an air-bath at a temperature of from 70° to 75° C. The complete drying of the film requires about twenty-six hours.

The percentage of alcohol is best determined by distillation. this purpose one hundred cubic centimetres of the beer are taken, a few drops of caustic soda added to neutralize the free acid, and the liquid brought up to about one hundred and fifty cubic centimetres. It is then distilled with the aid of a Liebig condenser into a graduated flask until nearly one hundred cubic centimetres have come over. The distillate is now thoroughly mixed, cooled to 15° C., and then brought exactly to the 100-cubic-centimetre mark and again mixed. Its specific gravity is now taken, and from a set of alcohol tables (see Hehner's tables, Appendix, p. 579) the percentage of alcohol by weight of the distillate found. Then as the specific gravity of the original sample is to the specific gravity of the distillate so is the weight per cent. in the distillate to the weight per cent. in the original sample. Indirectly the alcohol percentage can be determined, although not with the same accuracy, by the aid of the data gotten in the determination of extract already narrated. For if the specific gravity of the original sample be divided by the specific gravity of the de-alcoholized solution we get the specific gravity of the alcohol driven off, from which figure the percentage by weight of alcohol can be gotten in the tables. When both the alcohol and the extract percentage of a beer are known, by Balling's method the percentage of extract in the original wort can be calculated, and then with the aid of this and the percentage of extract in the beer the "attenuation" or diminution in the gravity of the original wort due to fermentation and alcohol production can be determined. As the weight of alcohol produced is approximately fifty per cent. of the saccharine matter destroyed by the fermentation, we have the formula 2a + e = w, in which a is the alcohol percentage, e the extract percentage of the beer, and w the percentage strength of the original wort. Then using this figure just obtained w:100::2a:x, in which x will represent the degree of attenua-More accurately, the actual degree of fermentation (Wirklicher Vergährungsgrad) is gotten by the proportion p: p-n::100: v', in which p is the extract in the original wort, n the extract in the beer, and v' the actual fermentation degree; (p-n) is termed the "real attenuation." It is obvious from the two proportions given that in practice 2a is often taken as equivalent to (p-n). This is not strictly correct. It is found in the fermentation of beer-worts that 100 parts of extract yield 48.391 parts of alcohol, so that what is termed an "alcohol factor" is necessary to convert one into the other. In England a different procedure is followed. A definite volume of beer is taken and one-half dis-This distillate is brought up with water at 60° F. to the original volume and its specific gravity taken. The difference between 1000 and the observed gravity is called the "spirit indication" of the beer. With this can be found, in a table prepared for the Inland Revenue Office, the "degrees of gravity lost" by the attenuation of the wort.

Then the liquid left in the retort after the distillation is diluted wi water and brought up to the original volume, when its specific gravity carefully taken. This is called the "extract gravity," and this added the degrees of gravity lost gives the "original gravity of the wort."

The acidity of beer is partly due to lactic and succinic acids, whi are fixed acids, and partly to acetic acid, which is volatile. The fixed acids are usually determined jointly in terms of lactic acid by dissolving the dry extract of the beer in water and titrating the solution with demormal alkali solution. Baryta-water is preferred by many chemists, the sulphate of baryta which forms carries down much of the coloring and allows the end reaction to be better seen. The volatile acid of be is chiefly acetic acid, which is usually determined by subtracting the measure of alkali required to neutralize the extract from that require by the original beer (after getting rid of the carbonic acid by shaking thoroughly).

The chief adulterations of beer are from the use of salicylic acid as preservative and the addition of various bitter principles as substitut for hop-bitters. The salicylic acid may be searched for by concentrating the beer to one-half at a gentle heat and shaking the cooled liquid with ether, or a mixture of ethylic ether and petroleum-ether. The ethere layer is then separated, evaporated to dryness, and the residue dissolve in warm water. On adding ferric chloride, a violet coloration is produced if salicylic acid be present. Other chemists recommend dialyzing when the salicylic acid will readily dialyze into the pure water and can then be tested. For the detection of the bitter principles used as substitutes for hops elaborate schemes have been proposed by Enders (give in Allen, 4th ed., vol. i, p. 162) and Dragendorff (Gerichtliche-Chemisel Ausmittelung der Gifte).

### C. THE MANUFACTURE OF WINE.

#### I. Raw Materials.

1. The Grape.—While the name wine is often used to include the products of the spontaneous alcoholic fermentation of any sweet fruit aberry, it is usually limited to the product of the fermentation of the grape, which alone is cultivated on an extensive scale throughout the civilized world purely for the manufacture of wine.

The cultivation of the grape-vine and the production of wine ther from dates back to the earliest historic times. Beginning in the Ea and the Mediterranean lands, it extended northward and westward unt at present France is the chief wine-producing country, while German Austria, Spain, and Portugal have all established flourishing wine it dustries indigenous to their soil. In this country, the wine industry mainly established in the States of Ohio, New York, Virginia, and Calfornia.

The varieties of the vine (estimated to number almost two thousand hitherto cultivated in Europe are all said to be derived from the sing

species, Vitis vinifera. In this country four or five wild species have yielded varieties which when cultivated have proven adapted to wine production. Thus Vitis riparia, or "frost-grape," has yielded as cultivated varieties the Taylor and the Clinton grapes; the Vitis astivalis, or "summer-grape," has yielded as varieties Norton's Virginia, Cythiana, and Herbemont; the Vitis Labrusca, or "Northern fox-grape," has yielded as varieties the Catawba, Isabella, Concord, and Delaware grapes; the Vitis vulpina or rotundifolia, or "Southern muscadine," has yielded as varieties the black, red, and white Scuppernong. Numerous varieties of the European vine, the Vitis vinifera, have also been cultivated successfully in California, among which may be mentioned the Mission, Riesling, Traminer, Rulander, Gutedel, and Zinfandel.

The grapes owe their wine-producing value in the first place to the grape (or invert) sugar which they contain, and in the second place to the free acids, which in the later ripening of the wine are to develop the fragrant ethers, and to the albuminoids, which exert a great influence on the fermentation. The composition of the grape varies of course in different localities and even from year to year in the same locality, but its mean composition is thus stated by König: Grape-sugar, 14.36 per cent.; free acid (tartaric), .79 per cent.; nitrogenous material, .59 per cent.; non-nitrogenous extract, 1.96 per cent.; skins and kernel, 3.60 per cent.; ash, .50 per cent.; and water, 78.17 per cent.

The grapes are taken for wine-making only when they are fully ripe, and in many localities it is even customary to wait until the grape shows a slight appearance of over-ripeness or evidence of wilting, so that the maximum of sweetness may be attained. In some cases the grapes are plucked from the stems, either by hand or by the aid of three-pronged forks, while in other cases the stems are left when they are crushed in order that the tannin so obtained may aid in the clearing of the fermenting juice. This juice is known as "must," and the pressed pulp and skins as the "marc."

2. The Must.—This may properly be considered as still a raw material, as its expression from the grapes is purely a mechanical process. This is now generally effected by power-presses of various forms, although at one time largely effected by trampling the grapes under feet. (This method is still followed in the Oporto and the Maderia wine districts.) The first portion of must that runs from the presses is often collected separately, as it is the juice of the ripest and sweetest grapes; that which comes later is richer in acid and in tannin, as it comes partly from unripe grapes and partly from the stems and skins. The amount of must that is obtained usually ranges from sixty to seventy parts in the one hundred of grapes.

The composition of this must is of the greatest importance, as upon it depends the character of the wine that will be produced, whether it shall ferment normally throughout and develop the perfect flavor and aroma desired, or whether it shall be thin and sour and show tendencies towards alteration or "disease." The proportions of its constituents, especially the grape-sugar, may vary within quite wide limits from year

to year, and in grapes grown in the same year under different condition of soil, exposure, etc.

Thus, two different musts of 1868 are given and two musts of t same variety of grape in two succeeding years, the first of which was favorable year and the second an unfavorable year. The analyses a all by Neubauer.

	Sugar.	Free acid.	Albumi- noids.	Ash.	Non-nitro- genous extract.	Wate
Neroberger Riesling, 1868 Steinberger Auslese, 1868	18.06	0.42	0.22	0.47	4.11	76.7
	24.24	0.43	0.18	0.45	8.92	70.7
	23.56	0.46	0.19	0.44	5.43	69.9
	16.67	0.79	0.88	0.24	5.17	76.8

The percentage of grape-sugar in the must sinks at times to twell per cent., and may rise as high as twenty-six to thirty per cent. The ratio between acid and sugar, according to Fresenius, ranges from 1:2 for good varieties of grapes in good years to 1:16 for inferior varieties in medium years. If the ratio falls as low as 1:10, the grapes are unripe and taste acid. This ratio of acid to sugar is now generally take as the criterion for the quality of the must in any year or special locality.

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In bad seasons the free acid is more generally malic than tartari which is the normal constituent.

# II. Processes of Manufacture.

1. FERMENTATION.—The fermentation of the must is a spontaneou one following exposure to the air, and due to the spores which dro upon the surface of the must as exposed in the fermenting-tubs. It ma be a surface fermentation, taking place at temperatures of 15° to 20° C as is the practice in Italy, Spain, and the south of France, or a bottom fermentation, taking place in cooler cellars at 5° to 12° C., as is th practice in Germany and with the finer French wines. The first metho produces a flery wine rich in alcohol, but without bouquet or aroma; th second method, lighter wines with delicate bouquet, due to the formatio of wine esters. In either case the fermentation can be divided, as we the case with malt liquors, into three stages: the first, or main ferments tion, which, according as the surface or the bottom fermentation metho is followed, lasts from three to eight days, or from two to four weeks the second, or still fermentation, which lasts until the following spring and the third, the storage fermentation, which lasts for several year until by the gradual development of its bouquet it becomes perfectl ripe.

In the case of red wines, the main fermentation is allowed to tak place with the marc added to the must, so that as the alcohol is develope it may dissolve out the coloring matter (œnocyanin) of the skins as we as some of the tannin, which latter is of benefit in effecting a more rapi separation of the protein materials. To prevent this pulpy mass from rising to the surface and starting a souring of the wine, perforate

covers are often used in this case to hold it down. In the main fermentation, the casks are usually freely exposed to the air. Many wine experts recommend in addition the aeration of the fermenting must or a whipping of the liquid, so as to induce a fuller and more vigorous fermentation. On the other hand, other authorities consider that this excessive exposure to air injures the quality and aroma of the wine, and recommend only a partial exposure to the air after the main fermentation has begun. As the main fermentation comes to an end, the yeast (with more or less tartar, gummy matter, and albuminoids) settles to the bottom, the liquid clears and is ready to be racked off into casks, under the name of young wine (Jungwein), to undergo the after- or stillfermentation. If the racking off does not take place promptly with the ending of the more energetic main fermentation, the young wine, of which a considerable surface is exposed to the air, is very apt to start into the acetic fermentation. The casks into which it is now put are kept quite full in order to prevent this undesirable change, slight additions being made every few days if necessary, and the bungs are set loosely in place. During this after-fermentation there deposits upon the inner walls of the cask argols, or impure acid potassium tartrate (Weinstein), with some yeast and albuminoid matter. This fermentation lasts from three to six months, and then the wine is racked off again into smaller casks to undergo the final ripening, in which the bouquet of the wine is especially developed by the formation of esters, while it clears more thoroughly from the remaining particles of yeast, etc. The duration of this ripening may be two, four, or with rich wines even eight years or more, when it is considered "bottle-ripe." During this ripening fungous vegetation is very apt to start, and must be arrested in order to prevent the spoiling of the wine.

2. DISEASES OF WINES AND METHODS OF TREATING AND IMPROVING THEM.—The souring of wine, due to the beginning of the acetic fermentation, is one of the commonest of these so-called diseases, especially with light wines, poor in alcohol and tannic acid, and hence commoner with white than with red wines. It arises from too free an exposure to the air and too high a temperature during fermentation. If just begun it can be cured by the addition of a small quantity of potashes, which form potassium acetate, or by starting the alcoholic fermentation afresh by adding a new quantity of sugar. If the souring is very pronounced it cannot be cured, and the wine is made into wine-vinegar.

The gumminess or ropiness of wine frequently arises from a premature filling into bottles, and is due to the beginning of the mucous fermentation of sugar. It takes place in wines poor in tannic acid, and hence more readily with white than with red wines. It can be cured by addition of tannic acid, treatment with sulphurous oxide, or starting a new fermentation by addition of grape-sugar.

The development of a stale or flat taste in the wine is due, according to Pasteur, to the growth of a thread-like ferment. The wine becomes cloudy, diminishes in alcohol and increases in acid percentage, it darkens in color, and often has a disagreeable odor. The wine is racked off and

put into a cask which has been filled with sulphurous oxide fumes, which destroy the ferment.

The turning bitter of red wines is due also, according to Pasteur, to a plant-growth, according to others to the formation of a bitter aldehyde resin. Neubauer has found that the tannic acid and the coloring matter both decrease in percentage in this disease. It can be cured completely by heating the wine to 60° to 64° C., or by starting the fermentation anew by adding fresh quantities of grape-sugar.

The mouldiness of wine is due to the development of a fungoid growth in the form of a white film on the surface of wines poor in alcohol, and always precedes the souring of the wine. It is to be obviated by treatment with sulphur dioxide or more effectual protection of the young wine from the air.

Of the general lines of treatment adopted to prevent the development of these various diseases, we notice first the clarifying with isinglass (finings) or other form of gelatine. This is particularly applied to the sweet and heavy white wines, which often remain turbid and have to be cleared by the coagulating of the albuminoid which is added. With red wines which contain tannic acid, casein or blood albumen is used instead of gelatine. Fine clays are also used, especially in Spain, for this clarifying.

The most important process, however, which is applied for the preservation and protection of wine against diseases is that known as "Pasteurizing." It consists in heating the wine either in casks or in bottles to a temperature of 60° C., and then preserving it without exposure to the air. This temperature is found to be sufficient to kill most of the germs which bring about the diseases before mentioned. A form of cask much used for this "Pasteurizing" process is shown in Fig. 60.

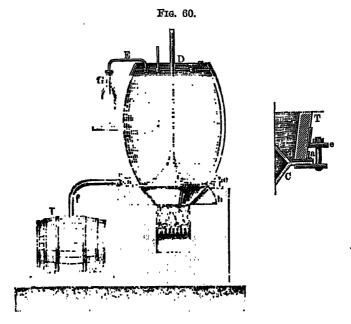
The use of salicylic acid for preserving wines has been extensively tried, but its use here is open to the same objection as before stated in speaking of beer, and it is now forbidden in most countries.

Of the methods of "improving" wines, as it is termed, that known as "plastering" is probably most largely practised, its use for red wines extending to Spain, Portugal, Italy, and the South of France. It consists in adding plaster of Paris (burnt gypsum) either to the unpressed grapes or to the must. The plaster takes up water and so increases the alcoholic strength of the fermenting must, which in turn allows of a greater extraction of the coloring matter from the skin. same time the wine is given better keeping qualities as well as deeper color. However, the sulphate of lime changes the soluble potash salts of the wine into insoluble tartrate of lime and soluble acid sulphate of potash, which latter remains dissolved along with some of the gypsum, and undoubtedly has an injurious effect upon the consumers of the wine. The process has hence had to be controlled by law, and in France the sale of wine containing over .2 per cent. of potassium sulphate is prohibited. The ash of pure wine does not exceed .3 per cent., but in the samples of sherry usually met with it reaches .5 per cent., and is almost entirely composed of sulphates.

Hugonneng recommends adding dicalcium phosphate instead of gypsum. This process, called "phosphotage," is said to have all the good effects obtainable from plastering without increasing, as the latter does, the percentage of sulphuric acid and decreasing that of phosphoric acid.

Chaptalization consists in neutralizing the excess of acidity in the must by the addition of marble-dust, and increasing the saccharine content by the addition of a certain quantity of cane-sugar, which the vintners sometimes replace by starch-sugar. In this process the quantity of the wine is not increased, but it becomes richer in alcohol, poorer in acid, and the bouquet is not injured. It is much used in Burgundy.

Gallization, as proposed by Dr. Gall, has for its object the bringing of the must of a bad year up to the standard found to belong to a good



must (he takes as standard 24 per cent. of sugar, .6 per cent. of acid, and 75.4 per cent. of water) by correcting the ratio of acid to sugar. This he does by adding sugar and water in sufficient quantity, and tables have been prepared to indicate the quantity needed according to the acid ratio shown by analysis. In both these processes, starch-sugar ought never to be used as a cheaper substitute for cane-sugar, as commercial starch-sugar will always introduce dextrine, an entirely foreign constituent, into the must.

Petiotization is a process which takes its name from Petiot, a proprietor in Burgundy, and is carried out as follows: The marc from which the juice has been separated as usual by pressure is mixed with a solution of sugar and water and the mixture again fermented, the second steeping containing, like the first, notable quantities of bitartrate of potash, tannic acid, etc., which are far from being exhausted by one extraction. The process may be repeated exeral times the different infusions

being mixed. This process is very largely used in France, and is said to produce wines rich in alcohol, of as good bouquet as the original wine, and of good keeping qualities. It is not allowed to be sold there, however, as *natural* wine.

Scheelization consists in the addition of glycerine to the finished wine so as to improve the sweet taste without injuring its keeping qualities. The limits of the addition of glycerine lie between one and three litres to the hectolitre of wine. If the wine has not fully fermented, however, and if yeast-cells are present, the glycerine may yield propionic acid by decomposition.

3. MANUFACTURE OF EFFERVESCING WINES (Champagnes).—For the manufacture of champagne the blue sweet grapes are preferred. must be pressed promptly after picking in order that the least possible amount of color be taken up by the must. The first pressing only is used for the champagne, and a second pressing of the marc yields a reddish wine, which is differently utilized. The must is first put into vats that impurities may settle and then filled into casks for the main fermentation, which is retarded as much as possible by being carried out in cool cellars. Cognac is also added to the amount of about one per cent. so as to increase the alcohol percentage and thus moderate the fermentation. After the main fermentation is finished the wine is racked off into other casks and left stopped until winter (end of December). It is then fined (or cleared) with isinglass and transferred to other casks, and this operation is repeated in a month's time. Towards the beginning of April it is ready to be transferred to bottles. The wines of different growths are now mixed and the amount of sugar in the wine determined, when a calculated additional quantity is added in the form of "liqueur" (a mixture of alcohol and pure cane-sugar). The bottles which are to receive the champagne must be specially chosen and be sufficiently strong to stand the pressure, which rises later to four to five atmospheres. They must also have sloping sides, so that the sediment may not adhere to the sides in the after-process. The wine after being corked is thoroughly secured by an iron fastening called an agrafe, and the bottles are arranged in piles in a horizontal position in the large champagne-vaults, where they remain throughout the summer months. Previous to the wine being prepared for shipment, the bottles are placed in a slanting position, neck downward, in frames, and the incline is gradually increased day by day until the bottle is almost perpendicular. With the sediment thus on the cork it goes into the hands of a workman called a "disgorger," who, holding the bottle still neck downward, proceeds to liberate the cork by slipping off the agrafe, and when the cork is three-fourth parts out he quickly inverts the bottle. The cork is thus forcibly ejected with a loud report by the froth, which carries with it the greater part of the yeast and other solid matters, what remains of these being got rid of by the workman working his finger round the neck of the bottle, whereby they are detached and forced out by the still rising froth. The wine is now dosed again with liqueur, the bottles filled up, wired, and the neck wrapped with foil ready for shipment.

4. MANUFACTURE OF FORTIFIED, MIXED, AND IMITATION WINES.—All

the sweet heavy wines, like sherry, malaga, and port, are characterized by a high alcohol percentage, ranging from sixteen to twenty or twenty-two. This they cannot acquire through fermentation alone, as twelve or thirteen per cent. seems to be the limit of alcohol developed in a wine by direct fermentation. They have the additional alcohol added to them directly in order to give them keeping qualities. With some sweet wines the alcohol is added to the must before the fermentation in order that the fermentation shall be arrested, while a certain amount of sugar remains in the wine unchanged. The quality of wines is often improved by blending. Light wines with too little alcohol are mixed with stronger wines with the formation of an excellent product with better keeping qualities, which can then be transported to long distances without injury. These mixtures can best be made when the wines are new, in order that after mixing they may undergo an insensible fermentation and take a character distinctive of the new product.

The practice of adding flavoring substances totally foreign to the constituents of the must to new and inferior wines in order that they may take the flavor and appearance of older and more valuable wine has also become very wide-spread. Such practices are of course illegal in all countries where laws against adulteration are enforced. Thus, elder flowers, orris-root, iris, cloves, oil of bitter almonds, and numerous perfumes, such as oil of orange flowers, of neroli, of petit-grain, and of violet, are used, as well as coloring infusions like raspberries and walnuts. The heavy wines are the ones most generally imitated. Port is frequently flavored with a mixture of elderberry juice, grape juice, brown sugar, and crude brandy. Sherry often consists of the cheaper Cape wine mixed with honey, bitter almonds, and brandy. In Spain and Southern France a wine prepared from the vine known as the *Teinturier* and possessing an intense bluish-red color is extensively used for coloring of other wines.

In recent years, because of the deficiency in the wine crop of France due to the ravages of the *Phylloxera*, the production of wine from dried raisins or prunes has enormously increased. This product, known as "vin de raisin sec," is said to be a very close imitation of natural French wines. Spon \* gives the following as the components of such a raisin wine:

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White sugar ... 5 kilos.

Raisins ... 5 kilos.

Common salt ... 125 grammes.

Tartaric acid ... 200 grammes.

Sommon salt ... 125 grammes.

Gall-nuts (bruised) ... 200 grammes.

Brewer's yeast (in paste) .200 grammes.
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To make this wine of a red color it is necessary only to add to the above ingredients two hundred and fifty to three hundred grammes of dry picked hollyhocks, taking care to keep them at the bottom of the cask.

The reports of the United States consular agents show that the manufacture of this raisin wine has become an industry of large proportions in France at the present time. A significant additional indication

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of the development of this artificial wine industry and of the simils one of petiotizing in France is found in the statement of the amoun of cane-sugar used by French wine manufacturers in recent years. I 1885 there was used in France for the manufacture of grape win 7,933,887 kilos. of cane-sugar; in 1886, 27,856,592 kilos.; for the manufacture of fruit wines in 1885, 24,142 kilos. of sugar; in 1886, for the same purpose, 145,555 kilos. Most of this fruit wine forms the bas of factitious champagne.

# III. Products.

The normal constituents of a natural wine agree of course with the contained in the must, except in so far as new compounds have bee developed by the fermentation process and previously existing ones habeen decomposed or made to separate out.

We may divide the constituents of wine into two classes, volatile ar fixed. The volatile matters are as follows: Water (eighty to ninety potent.); alcohol (five to fifteen per cent.); glycerine (two to eight potent.); volatile acids, acetic, cenanthic, etc., constituting one-fourth one-third of the total acidity; aldehyde, compound ethers, together wis other fragrant indefinite constituents, which give the wine its flavor at bouquet. The fixed matters are glucose, or grape-sugar, in small quatities in most wines; bitartrate of potash, tartaric, malic, and phosphor acid, partly free and partly combined with various bases, of which cor pounds phosphate of lime is the most abundant, constituting from twenty to sixty per cent. of the weight of the ash, the remainder being chiefly carbonate of potash, resulting from the calcination of the bita trate, with a little sulphate and traces of chlorides; coloring matter pectin and analogous gummy matters; tannin, one to two per cent. The red wines and traces only existing in white wines.

No very simple scheme of classification is possible, as the methor and products of most countries are not fixed by rule, but vary wide according to the season and market. Still, we may distinguish between the red and white, and the sweet and the dry, wines; between the light and delicately-flavored German and French wines and the more field but coarser Italian and Swiss wines; between natural wines and tho fortified by addition of alcohol, as port, sherry, and madeira; between still wines and effervescing or champagne wines.

Most of these terms have already found their explanation in the description of the processes of manufacture. We may add that a swe wine is one in which a notable portion of the original grape-sugar of the must have escaped fermentation, or to which an addition of sugar have been made subsequent to the main fermentation. A dry wine, on the contrary, is one in which the sugar, whether originally present or su sequently added, has almost all undergone change in the processes of fermentation. Champagnes are wines in which a supplementary ferme tation is purposely developed subsequent to the bottling, where quantities of carbon dioxide gas are developed and held dissolved und pressure. On opening the bottles and thus relieving the pressure a bri effervescence follows, due to the escape of the absorbed gas. Champagn

makers distinguish three grades of effervescence. In mousseux the pressure in the bottles amounts to from four to four and a half atmospheres; in grand mousseux it reaches five atmospheres; and less than four atmospheres' pressure constitutes cremant (from la crème, "cream"), a wine which throws up a froth, but does not give off carbonic acid violently. Some manufacturers also distinguish a grade demi-mousseux.

Of natural and unfortified foreign wines the following analyses from Elsner \* refer to German wines exclusively:

	Specific gravity.	Percentage of alcohol.	Percentage of extract.	Percentage of free acid (as tartaric).	Percentage of ash.	Percentage of phosphoric acid.
Rhine wines, Rüdesheimer	0.9960 0.9960	9.30 9.25	1.97 2 10	0.50 0.54	0.20 0.19	0.020 0.023
" Johannisberger	0.9958	8.60	2.20	0.52	0.19	0.028
" " Hochheimer	0.9985	8.00	1.50	0.72	0.16	1 1
" " Niersteiner	0.9956	7.54	1.75	0.62	0.18	0.012
Moselle wines, Brauneberger			2.60		0.18	0.041
" " Pisporter			2.40		0.15	0.038
_ " " Zeltinger			2.40	• •	0.16	0.089
Hessian wines, Bodenheimer	0.9930	7.54	1.25	0.63	0.14	
" " Laubenheimer	0.9984	6.83	1.00	0.60	0.10	
" " Liebfrauenmilch .	0.9940	8.00	1.96	0.62	0.20	[ · · · ]
Palatinate wines, Deidesheimer .	0.9968	9.60	2.12	0.50	0.18	
" " Oppenheimer .	0.9985	8.87	1.50	0.60	0.16	
" " Wachenheimer.	0.9954	8.65	1.72	0.65	0.17	1 [
Franconian wines, white	0.9943	6.65	1.20	0.60		0.015
" " red	0.9932	8.00	1.50	0.47	0.20 .	
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The following analyses of French wines are from the official report of the Laboratoire Municipal at Paris for 1883: †

		Grammes per Litre.						
	Alcohol by volume.	Extract at 100° C.	Extract in vacuo.	Ash.	Tartar.	Reducing sugar (as glucose).	Sulphate of potash.	Acidity (in H <sub>2</sub> SO <sub>4</sub> ).
Bordeaux wines, St. Estephe, 1878  " " Medoc, 1880  " " Latour, 1878  " " Chateau Margaux, 1878  " " Larose, 1877  " " (white,) Sauterne, 1880  Burgundy wines, Chambertin, 1882  (white,) Chablis, 1878  Lower Burgundy, average of 7 analyses  Upper Burgundy, average of 25 analyses	11.1 10.3 9.5 10.2 11.2 10.4 11.5 11.0 7.8 9.1	22.4 19.0 17.0 28.6 28.0 16.0 28.3 16.7 20.2 20.7	28.3 28.7 22.8 30.1 29.5	2.20 2.05 2.14 2.84 1.77	1.81 1.42 2.07 2.44 8.57	1.50 0.9 1.1 1.5 1.8 8.6 1.4 0.6 1.2 1.1	0.49 0.76 0.50 0.48 0.63 0.53 0.55 0.38 0.37 0.48	2.96 8.96 4.06

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<sup>\*</sup> Praxis des Nahrungsmittels Chemiker, 1880, p. 103.

<sup>†</sup> Deuxième Rapport du Laboratoire Municipal, Paris, 1884.

Of sweet and fortified or treated wines the following analyses are given by König:\*

	Specific gravity.	Alcohol by weight.	Extract.	Sugar.	Tartaric acid.	Glycerine.	Albuminoids.	Ash.	Phosphoric acid.	Sulphuric acid.
Tokay, 1868 Tokay, Ausbruch, 1866 Ruster, Ausbruch, 1872 Malaga, 1872 Muscat wine, 1872 Port wine (white), 1860 Port wine (red), 1865 Marsala (Ingham) Marsala (Woodhouse) Madeira, 1868 Sherry, 1870 Sherry, Amontillado, 1870 Samos wine, 1872	1.0879 1.0588 1.0849 1.0691 1.0574 1.0125 0.9966 1.0111 1.0018 0.9952 0.9924 1.0519	9.80 10.29 8.96 13.28 10.02 16.28 17.93 16.78 15.52 15.34 18.66 16.84 10.97	26,36 18,34 28,64 21,23 16,91 8,83 4,94 5,45 5,33 8,78 2,68 14,46	22.11 14.99 21.74 16.57 15.52 4.88 6.42 3.78 3.78 3.39 1.88 0.52 11.82	0.509 0.517 0.512 0.416 0.555 0.451 0.896 0.470 0.489 0.438 0.490 0.502	0.212 0.234 0.162 0.248 0.298 0.145 0.298 0.457 0.291 0.506 0.560	0.427 0.389 0.281 0.217 0.151 0.094 0.200 0.281 0.144 0.200 0.200 0.287	0.343 0.300 0.409 0.239 0.312 0.236 0.270 0.418 0.376 0.483 0.650 0.563	0.050 0.074 0.057 0.042 0.036 0.035 0.024 0.024 0.024 0.082 0.032 0.038 0.058	0.061 0.022 0.035 0.026 0.073 0.039 0.019 0.087 0.155 0.081 0.184 0.268 0.044

Two analyses of champagne and effervescing wine are also given by König: †

	Specific gravity.	Alcohol by weight.	Extract.	Sugar.	Tartaric acid.	Glycerine.	Albuminoids.	Ash.	Phosphoric acid.	Sulphuric acid.
Champagne, Carte Blanche Effervescing Rhine wine	1.0488	9.51	13.96	11.53	0.581	0.084	0.219	0.184	0.027	0.017
	1.0874	9.80	10.88	8.49	0.566	0.062	0.294	0.171	0.034	0.026

Of American wines a large number have been investigated by the United States Bureau of Agriculture. A selection from those analyzed by H. B. Parsons ‡ in 1880 is given:

,	Specific gravity.	Alcohol by weight.	Alcohol by volume.	Extract.	Ash.	Glucose.	Total acid as tartaric.	Fixed acids as tartaric.	Volatile acid as acetic.
Dry red wines: Conco Clinto Nortol Ives's Sonoma Red Mission, California, 1879 Sonoma Red Zinfandel, California, 1879 Concord Bouquet, New Jersey	0.9958	8.88	11.08	2 10	0.174	Trace.	0.709	0.452	0.206
	0.9950	9.82	12.31	2.86	0.238	None.	0.784	0.518	0.217
	0.9987	10.21	12.77	2.88	0.298	Trace.	0.772	0.377	0.316
	0.9944	8.68	10.82	2.18	0.247	Trace.	0.723	0.512	0.169
	0.9968	7.99	10.08	2.42	0.428	None.	0.722	0.301	0.337
	0.9962	7.80	9.78	2.43	0.255	Trace.	0.693	0.391	0.242
	0.9928	9.84	12.31	2.18	0.141	0.71	0.741	0.272	0.375

<sup>\*</sup> Nahrungs- und Genussmittel, vol. ii, p. 463.

<sup>†</sup> Ibid., p. 464.

<sup>‡</sup> United States Bureau of Agriculture, Bulletin No. 13, pp. 334-338.

	Specific gravity.	Alcohol by weight.	Alcohol by volume.	Extract.	Ash.	Glucose.	Total acid as tartaric.	Fixed acids as tartaric.	Volatile acid as acetic.
Dry white wines: Brocton Catawba, New York Missouri Catawba, Missouri Ohio Catawba, Ohio Ruländer, Virginia, 1880  880  880  Riesling, California, 1879 Sweet Missouri Angeles, California, 1879 Sweet Marses Brocton Port, New York Speer's Port, New Jersey Fort, Los Angeles, California New York Sherry Speer's Sherry, New Jersey California Sherry Marsala, California  "Eclipse" Extra Dry Champagne "Gold Seal" Champagne, New York Cook's "Imperic" Sweet Catawba, Sweet Catawba, Sweet Catawba, Sweet Muscatel, California  Scuppernong, Sweet, 1878 Scuppernong, Dry, 1879	0.9890 0.9911 0.9892 0.9914 0.9982 0.9928 0.9928 0.9928 0.9929 1.0508 1.0208 1.0208 1.0207 1.0074 1.0402 1.0402 1.0402 1.0207 1.0402 1.0207 1.0207 1.0388 1.0512 1.0404 1.	12 28 8.88 9.88 9.55 10.46 9.55 10.46 9.55 10.46 9.55 10.37 7.78 9.52 49.56 10.00 10	15.30 11.08 11.08 11.70 12.77 13.05 11.70 9.80 9.80 11.295 11.44 11.265 11.70 10.82 11.759 16.52 22.09 10.82 11.87 11.85 11.85 11.87 11.85	2.09 1.67 1.68 1.89 1.60 1.82 1.47 1.72 1.72 1.74 1.74 1.75 1.70 1.70 14.18 8.48 9.91 14.77 14.49 16.71 14.49 16.71 14.49 16.71 14.49 16.72 14.49 16.72 14.49 16.72 16.5	0.121 0.129 0.199 0.255 0.146 0.185 0.146 0.180 0.180 0.180 0.180 0.180 0.180 0.180 0.180 0.190 0.221 0.196 0.221 0.196 0.219 0.196 0.219 0.196 0.219 0.196 0.219 0.196 0.219 0.196 0.219 0.196 0.219 0.196 0.219 0.196 0.219 0.196 0.219 0.196 0.219 0.196 0.196 0.219 0.196	Trace. Trace. Trace. Trace. None. Trace. Trace. Trace. Trace. Trace. Trace. 11.89 4.84 8.38 2.20 7.28 11.00 15.22 4.51 12.48 15.31 10.27 11.56	0.542 0.772 0.728 0.545 0.662 0.619 0.592 0.786 0.792 0.593 0.476 0.593 0.476 0.689 0.476 0.573 0.692 0.476 0.693 0.478 0.693 0.478 0.693 0.478 0.693 0.478 0.693 0.478 0.793	0.470 0.887 0.424 0.302 0.317 0.302 0.212 0.212 0.217 0.600 0.217 0.487 0.499 0.271 0.470 0.470 0.471 0.470 0.470 0.471 0.490 0.471 0.490 0.471 0.490 0.471 0.490 0.471 0.490 0.471 0.490 0.471 0.490 0.471 0.490 0.400 0.400 0.400 0.400 0.400 0.400 0.400	0.068 0.308 0.248 0.194 0.182 0.208 0.289 0.290 0.389 0.411 0.242 0.182 0.128 0.128 0.128 0.166 0.472 0.346 0.247 0.247 0.249 0.241 0.242 0.348 0.328

Side-products.—The first of these is the marc of the grapes, separated from the must in the original pressing of the grapes, or left when the fermenting must is drained from it. This consists of the stems, skins, and stones of the grapes. If the marc instead of being washed out with water has been merely pressed, it still contains sufficient must to allow of its being used in the manufacture of petiotized wine. Besides this, the marc serves for a great variety of purposes. It is fermented for brandy; it is used with sheet-copper in the manufacture of verdigris; it is used to start the fermentation in vinegar-making; as cattle-food; when dried, as fuel or for fertilizing purposes; the tannic acid is extracted, or it is used direct in producing black colors, and for other minor applications.

The second and more valuable side-product is the deposit formed on the bottom and sides of the casks in which the fermentation takes place. That on the bottom of the casks is called "lees." It contains from thirty to forty per cent. of vegetable matter (from the yeast-cells depositing), the remainder being tartrates, sulphates (in plastered wines), alumina, phosphoric acid, etc. Its composition is greatly altered by "plastering" the wine, in which case the tartrate exists chiefly as the neutral calcium tartrate instead of the acid potassium salt. The crystalline crust that forms on the sides of the vessels used for fermentation is called "argol," or crude tartar. It varies somewhat in composition, the tartaric acid

ranging from forty to seventy per cent. and being always present, chiefly as the acid potassium tartrate. From this crude tartar is prepared, by extraction with boiling water, filtering, and crystallizing, "cream of tartar." This, however, still contains some calcium tartrate mixed with the acid potassium salt, the amount ranging from two to nine per cent.

# V. Analytical Tests and Methods.

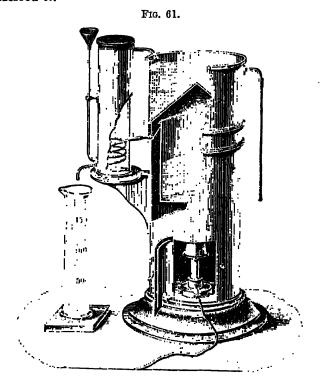
In 1884 the Imperial German Health Office appointed a commission of experts to report upon the best uniform methods for the analysis of wines. The methods agreed upon by that commission are very generally adopted now in Germany, and largely used elsewhere in guiding wine analysts. These official methods have been fully described and explained in a little work entitled "Weinanalyse," by Dr. Max Barth, Leipzig, 1884.

The specific gravity of the wine is determined either by the pyknometer (specific gravity bottle) or by the Westphal balance (see p. 87), the readings of which have been compared with those of the specific gravity bottle. In the case of champagnes and effervescing wines, as was the case with beer, the carbonic acid must be got rid of as far as possible before taking the specific gravity readings.

The alcohol is determined by the direct distillation, as described on Wines that have a tendency to foam have a little tannin (.1) gramme) added. If one hundred cubic centimetres of the sample is taken, sixty cubic centimetres only need be collected, and will contain all the alcohol. This is then diluted to nearly one hundred cubic centimetres, cooled, uniformly mixed, and then brought exactly to the 100cubic centimetre mark, mixed again, and the specific gravity taken. The form of apparatus best adapted for this determination of alcoholic strength of wines and liquors is shown in Fig. 61. For the rapid determination of the alcoholic strength of wines various forms of apparatus have been devised, such as the vaporimeter of Geissler, in which the vapor-tension of an alcoholic liquid exerted upon a column of mercury is made to indicate its percentage strength in alcohol, the ebullioscope of Tabarie, of Malligand and Vidal, and of Amagat, which depend upon the observation of the boiling-points of a spirituous liquor as determining the amount of alcohol contained. None of these can be said to have scientific accuracy, as wine is not merely a mixture of alcohol and water. but contains other constituents which affect the results in either case.

The extract detemination. Here the direct weighing of the residue after evaporation is preferred to the indirect method, fifty cubic centimetres of the wine, measured at 15° C., are to be evaporated on the water-bath in a platinum dish (according to the German wine commission, this dish should be eighty-five millimetres in diameter, twenty millimetres in height, seventy-five cubic centimetres in capacity, and should weigh about twenty grammes), and the residue dried for two and a half hours in a double-walled water drying oven. In the case of wines

containing more than .5 per cent. sugar, a smaller quantity must be taken and suitably diluted, so that the extract shall not weigh more than 1.0 to 1.5 grammes. In this method, the loss of glycerine by evaporation is trifling. The indirect method for determining the extract is very like that described under beer (see p. 221) as O'Sullivan's method, except that with wine we divide the excess of specific gravity observed over 1000 by 4.6 instead of 4, as the solids of wine have a higher solution density than those of extract of malt. Or with the specific gravity of the de-alcoholized liquid we may get the extract percentage from Hager's tables, which are analogous to those of Schultze for malt extracts before referred to.



The ash percentage can be obtained by incineration of the evaporated extract above referred to.

To determine the percentage of glycerine, one hundred cubic centimetres of the wine are evaporated down to about ten cubic centimetres in a spacious porcelain dish; some sand and milk of lime are then added till the reaction is strongly alkaline and the mixture evaporated almost to dryness. The residue is next treated with fifty centimetres of ninety-six per cent. alcohol, warmed and stirred on the water-bath, and the solution obtained then passed through a filter. The insoluble matter is washed with successive small portions of hot alcohol (ninety-six per cent.), of which fifty to one hundred and fifty cubic centimetres will as

a rule suffice, so that the entire filtrate will be from one hundred cult centimetres to two hundred cubic centimetres. The alcoholic extract now evaporated to a viscous consistency, and the residue taken up witten cubic centimetres of absolute alcohol; this solution is mixed wififteen cubic centimetres of ether in a stoppered flask and the mixtuallowed to stand until clear. The clear liquid is decanted or filtered in a light tared glass vessel, carefully evaporated, and the residue dried fone hour in the water-bath. It is then cooled and weighed. In the case of sweet wines (containing more than five per cent. of sugar), only fif cubic centimetres of the wine are taken for the estimation of the glastic centimetres of the wine are taken for the estimation of the glastic. After cooling it is treated with one hundred cubic centimetres ninety-six per cent. alcohol, the precipitate formed allowed to settle, the solution filtered, the insoluble matter washed with spirit, and the alcohol filtrate treated as above described.

To estimate the *sugar* in wine, Fehling's solution is used, as the sugshould be only glucose. After neutralization of the wine with sodiu carbonate, the determination is made (using the separately preserve solutions for Fehling's mixture. See p. 175). Strongly-colored win must be first decolorized. If the sugar percentage is low, it is done with purified bone-black; if they contain over .5 per cent. of sugar, bone-black cannot be used because of its absorptive power, and basic acetate of lease must be substituted. After filtering, the wine is then treated with sodiu carbonate and Fehling's solution. If the polarization indicates the preference of cane-sugar, the solution must be inverted (see p. 174) and the the Fehling's test applied again, and the cane-sugar calculated from the difference in the two readings. The Fehling's test is best carried or gravimetrically, and from the weight of reduced copper the corresponding amount of glucose can be obtained from the tables.

The polarization, which is essential in the case of heavy wines to inceate the nature of the sugar contained, is carried out as follows: Wi white wines, to sixty cubic centimetres of the wine are added three cubic centimetres of the basic acetate of lead solution and the precipita filtered off on a dry filter. To 31.5 of the filtrate is added 1.5 cubic centimetres of a saturated solution of sodium carbonate and the solution again filtered and the polarization tube filled with the filtrate. The diltion of the original wine in this case is 10:11. With red wines, six cubic centimetres of the wine are treated with six cubic centimetres the lead solution, and to thirty-three cubic centimetres of the filtrathree cubic centimetres of the saturated sodium carbonate solution adde the solution filtered and polarized. The dilution here is 5:6. The diluted solution is observed in the 220-millimetre tube of the polariscon and large and accurate instruments are necessary.

The free acids (total acid-reacting constituents of the wine) a estimated in twenty-five cubic centimetres of the wine heated to incipie boiling by means of one-tenth normal alkali. Any considerable quanti of carbonic acid to be first removed by shaking. The "free acids" to calculated into and given as tartaric acid  $(C_4H_6O_6)$ .

The volatile acids are determined by steam distillation and calculated as acetic acid  $(C_2H_4O_2)$ .

The quantity of non-volatile acids calculated as tartaric is found by subtracting the equivalent of the acetic acid in tartaric acid from the free acids previously determined.

These three determinations are all that are usually made in wine analyses. If a special qualitative test for free tartaric acid is desired or, in case it be shown to be present in appreciable quantity, a quantitative method for its determination, they can be made by Nessler's method, for details of which the reader is referred to Barth's "Weinanalyse" before mentioned, or to a summary of its methods in the "Journal of the Society of Chemical Industry," 1885, p. 553.

The tannin may be determined by Neubauer's method with permanganate of potash, or approximately by the following procedure: the free acids in ten cubic centimetres of the wine are neutralized with standard alkali, after which one cubic centimetre of a forty per cent. solution of sodium acetate is added, and finally a ten per cent. solution of ferric chloride, drop by drop, and avoiding excess. One drop of this solution suffices for the precipitation of every .05 per cent. of tannin.

Salicylic Acid.—To detect this acid, one hundred cubic centimetres of the wine are shaken repeatedly with chloroform, the latter is evaporated, and the aqueous solution of the residue tested with very dilute ferric chloride solution. For the purpose of an approximate quantitative estimation, it is sufficient, on the evaporation of the chloroform, to once recrystallize the residue from chloroform and weigh it.

One of the most important questions that arises in the examination of red wines is as to the genuineness of the coloring matter, as both vegetable and artificial dye colors have been used for years to imitate the natural coloring matter in the manufacture of factitious red wines. Very elaborate schemes for the recognition of foreign coloring matters, including both the vegetable coloring matters like dye-woods and color-yielding berries and the large number of the newer coal-tar colors, have been given by Gautier \* and by Chas. Girard, † the director of the Laboratoire Municipal in Paris, to which we can only give references. The coloring matters most generally used to imitate the natural pigment of the grapeskins are fuchsine, cochineal, alderberry, hollyhock, and logwood. Dupré tests the coloring matter as follows: Cubes of jelly are prepared by dissolving one part of gelatine in twenty parts of hot water and pouring the solution in moulds to set. These are immersed in the wine under examination for twenty-four hours, then removed, slightly washed, and examined. Pure wine will color the gelatine only very superficially: the majority of other coloring matters (fuchsine, cochineal, logwood, Brazilwood, litmus, and indigo) penetrate more readily, passing to the very centre of the cube. The double dyeing test of Sostegni and Carpentierit is now very frequently employed. Take one hundred cubic centimetres

<sup>\*</sup> Wynter Blyth, Foods, Composition and Analysis, p. 464.

<sup>†</sup> Deuxième Rapport du Laboratoire Municipal, p. 272.

<sup>‡</sup> Bulletin No. 107 (revised), Bureau of Chem., U. S. Dept. of Agric., p. 190.

of the wine, acidify with from two to four cubic centimetres of a ten per cent. solution of hydrochloric acid. In this solution immerse a piece of woolen cloth which has been washed in a very dilute solution of boiling potassium hydroxide and then washed in water and boil for from five to ten minutes. Remove the cloth, thoroughly wash it in water and boil in a very dilute hydrochloric acid solution. After washing out the acid dissolve the color in a solution of ammonium hydroxide (1:50). the wool out, add a slight excess of hydrochloric acid to the solution, immerse another piece of wool and boil it again. With vegetable coloring matter, such as the wine color, this second dyeing gives practically no color, and there is no danger of mistaking such a color for one of coal-tar origin which dyes the second piece of wool a bright shade. This test will detect minute quantities of fuchsine or aniline red. The fact that pure wine color is not changed or decolorized by nascent hydrogen (zinc and acid), while most of the aniline dyes are decomposed by it, is also used as a test.

# D. MANUFACTURE OF DISTILLED LIQUORS, OR ARDENT SPIRITS.

This industry differs radically from the two fermentation industries already described, firstly, in that the effort is made to push the fermentation to the fullest possible limit, so that the maximum quantity of alcohol may be produced, and, secondly, in that this product of fermentation is then distilled, and it may be redistilled in order to get a distillate richer in alcohol than the fermentation product itself can be. The end to be attained may be either the production of an alcoholic beverage as the product of distillation or of raw spirit, which takes name from the material used, as "grain spirit," "potato spirit," "corn spirit," etc. From this raw spirit by the processes of rectification is obtained the "rectified spirit" used as the basis of the manufacture of various alcoholic beverages and as a solvent in various manufacturing processes, and by purification and dehydration the absolute ethyl alcohol of the chemist.

#### I. Raw Materials.

These may be divided into three classes: First, alcoholic liquids, themselves the product of fermentation,—these require only to be submitted to distillation in order to yield the stronger spirit; second, solid and liquid materials containing some variety of sugar, whether cane-sugar, grape-sugar, or maltose, which are directly or indirectly fermentable; and, third, starch-containing cereals and all materials capable under the influence of diastase or dilute acids of hydrolysis and the production of a fermentable sugar.

1. Alcoholic Liquids (Wines).—The distillation of wines is followed for the production of an alcoholic beverage (brandy) which takes to some degree its flavor and bouquet from the wines used in the distillation. While factitious brandies are largely made from grain or potato spirit, the true product from wine is always regarded as superior.

The manufacture of wine brandy has been chiefly carried out in France, and in minor degree in Spain and Portugal. Within recent years California wines have also been used for the manufacture of brandies. The French wines which are used are largely those of the departments Charente and Charente-Inférieure, in the southwest of France, and the product is all known as Cognac brandy.

White wines are said to yield a superior spirit to that obtained from red wines, and older wines better than newer ones. About eight and a half hectolitres of wine are needed to produce one hectolitre of brandy. Because of the ravages of the Phylloxera insect, the manufacture of genuine wine Cognac has decreased enormously in France in recent years, while the manufacture of factitious Cognac has correspondingly increased. Thus we find it officially stated \* that the production of alcohol from wine in France had decreased from 530,000 hectolitres in 1875 to 14.678 hectolitres in 1883.

The marc of the grapes, as already stated (see p. 234), is also utilized in the manufacture of an inferior grade of brandy, known in France as eau de vie de marc. The lees, or sediment, of the wine-casks are also used in this same way. This brandy is not necessarily sold for consumption, but is used to strengthen the alcoholic percentage of wines in which fermentation is to be arrested.

2. Sugar-containing Raw Materials.—The most important sugaryielding materials cultivated on a large scale, it will be remembered, are
the sugar-cane and the sugar-beet. The sugar-canes are not used directly
for the production of spirits (except in the case of accidental souring),
and the "bagasse," although still containing saccharine juice, is too
bulky, and hence is at once burned as fuel, but the molasses obtained on
so large a scale in the extraction of raw sugar is a most valuable material
for the purpose. Throughout both the West Indies and the East Indies
enormous quantities of this molasses are fermented and the resultant
product distilled for rum. Even the sugar scums obtained in the defecating and concentrating of the sugar juice are fermented, and produce
an inferior grade of rum.

With the sugar-beet, both the beet itself and the beet-molasses are utilized, the former being used in France and the latter in both France and Germany. Sweet fruits, the juice of which is rich in sugar, also serve as raw materials for the spirit industry. Thus peaches, plums, and cherries are much used in different countries for the manufacture of fruit brandy, and the fermented juice of the date-palm in the East Indies and of the plantain in the West Indies both serve for the distillation of an alcoholic beverage.

3. STARCH-CONTAINING RAW MATERIALS.—This list includes the main sources for the distillation of spirits, as the high percentage of starch in many cereals, ranging from sixty to seventy-seven per cent., the ease with which the starch can be converted into fermentable sugar under the influence of diastase or dilute acids, and the cheapness of these starchy products of nature all combine to make them for most countries the

<sup>\*</sup> Deuxième Rapport du Laboratorie Municipal, p. 272.

cheapest and best materials for the spirit industry. In the United Statthe three cereals used almost exclusively for the manufacture of distill liquors are corn, rye, and malted barley; in England, barley, both reand malted, rye, corn, and rice; in Germany the potato is almost the on starchy material used. The composition of the several cereals shown their relative percentage of starch was given on p. 186.

## II. Processes of Manufacture.

1. Preparation of the Wort.—In England and the United State where grain spirit is mainly manufactured, the first process is that saccharifying the starch of the grain. In the special cases where malte grain alone is used, the mash process somewhat resembles that alread described under beer-brewing. Most distillers, however, use mixtures raw and malted grain, in which the raw largely predominates, being ofte ten to one or even more, as a very small quantity of diastase can be made to convert a large amount of starch into maltose or fermentable suga It is stated, moreover, that the yield of spirit is larger when several kind of grain are mixed than when one kind is used singly. The mixture ( raw and malted grain, properly ground, is put into the mash-tub (se Fig. 59, p. 214) with water at 150° F. and agitated. This first mashir requires from one to four hours, the larger the quantity of raw grain use the longer being the time required for mashing. The temperature of tl mixture is kept up to about 145° F. by the successive additions of wat at a somewhat higher temperature (190° to 200° F.). The object of the distiller in this is somewhat different from that of the beer-brewer. I wishes to convert the whole of the starch, if possible, into maltose, which is directly fermentable by the action of yeast, while the dextrine is no so he must mash at not much over 146°, which it will be seen from Fi 58 (p. 207) is the limit above which the maltose production begins When the gelatinization of the starch is complete, the ter perature of the mash may go slightly higher. By keeping within th limit of temperature, a minimum of diastase from the small admixtu of malt will gradually change not only the starch, but bring about hydration of the residual dextrine, converting it into maltose. the wort has acquired its maximum density, as found by the sacchar meter, it is drawn off, and fresh water at about 190° F. is run upon t residue in the mash-tub and allowed to infuse with it for one or tv This second wort is then added to the first. A third weak wo is often obtained, and used to infuse new lots of grain. The mash is the cooled down promptly to the temperature required for fermentation that the acetous fermentation may not set in.

It is stated that in this method of open-tub mashing ten per cent. the starch escapes decomposition, even although the grain may be takefinely ground. Hence a preliminary warming with water to which a litt green malt is sometimes added, followed by heating with water under pressure of several atmospheres, now often precedes the addition of t main quantity of the malt, which is to complete the conversion of t

starch and dextrine into maltose. This treatment is carried out in so-called "vacuum cookers."

In Germany potatoes constitute the chief raw material for the spirit manufacture. They contain from eighteen to twenty per cent. of starch only, however, while the cereals contain over sixty per cent. The amount of the malt needed for the saccharification of the starch can therefore be correspondingly reduced. Instead of mashing the ground, rasped, or chipped potatoes in open mash-tubs as was formerly done, they are now first steamed under a pressure of two to three atmospheres, whereby the starch-containing cells are thoroughly ruptured and the starch put in condition to be easily acted upon by the diastase. Among the forms of apparatus based upon this principle may be mentioned those of Hollefreund. Bohm. Henze, and Ellenberger. In that of Henze, which has been largely adopted, the potatoes, after steaming under a pressure of several atmospheres, are so disintegrated that on opening a valve in the bottom of the vessel the pulp is forced out through a grating in a thin This is cooled, mixed with the requisite quantity of malt, and started to mashing. In the Hollefreund and in the Bohm cookers, the steaming, disintegrating, and mashing all take place in the same closed vessel, the malt being added after the disintegrated mass has been properly cooled down. Green malt is found to work better in this case than air malt, and produces more alcohol.

2. FERMENTATION OF THE WORT, OR SACCHARINE LIQUID.—In the case of mashing, as described above, either with grain or with potatoes, the wort must first be cooled down before adding the yeast and starting the fermentation. The yeast used is a surface yeast, and either fresh brewer's yeast or compressed yeast (previously softened in warm water) may be used. The procedure is now somewhat different, according as we have a grain-mash or a potato-mash to deal with. In the former case, using a thin wort drained from the exhausted grain, it has been found that the best results are obtained when the temperature during fermentation rises to about 33° or 34° C. (92° to 94° F.), as shown in Fig. 58 (see p. 207); in the latter case, where the entire mash, solid matter and all, is fermented, the fermentation begins at a much lower temperature, and the heat evolved in the fermentation of such a concentrated wort ultimately carries the temperature to the same maximum. In the English plan, considerable lactic acid forms because of the higher temperature, and this constitutes a sour yeast mash, while in the German plan, because of the low initial temperature of the fermentation, comparatively little lactic acid is produced, and when the higher temperatures are reached the mixture already contains so much alcohol that the lactic acid ferment grows with considerable difficulty.

For one thousand litres of grain-mash, eight to ten litres of brewer's yeast or one-half kilo. of compressed yeast are used; for one hundred litres of potato-mash, one to two litres of brewer's yeast or three-fourths to one kilo. of compressed yeast are needed.

The fermentation is sometimes divided into several stages: the *pre-liminary* fermentation, in which the yeast-cells grow without much alco-

hol formation; the *main* fermentation, in which the maltose is fermented; and the *after*-treatment, in which the dextrine is gradually changed into maltose and this into alcohol.

The time of fermentation varies from three to nine days, but it is carried on until the density of the liquid ceases to lessen or attenuate, which is determined by the saccharometer.

The coefficient of purity of a fermentation is a term used to designate what percentage of the available starchy material in a substance has actually undergone the pure alcoholic fermentation. Thus, the reaction  $C_0H_{10}O_5+H_2O=2C_2H_6O+2CO_2$  demands from one kilogramme of starch a percentage of alcohol equal to 71.7 litres, and such a yield from one kilogramme of fermented material would indicate a purity coefficient of one hundred per cent. A percentage yield equal to sixty litres of alcohol from one kilo. of material would give a purity coefficient of 83.7 per cent.

The use of hydrofluoric acid or ammonium fluoride, first proposed by Effront as an antiseptic and indirect aid to the alcoholic fermentation, has become quite important in the spirit industry. The advantages claimed for its use are: first, by preventing the losses due to secondary fermentation, the alcohol yield is increased; second, this yield is especially maintained when raw materials of somewhat inferior quality are used, when without the hydrofluoric acid the yield would be diminished; third, the development of foaming in the fermentation is in large degree prevented.

In France, the juice from inferior beets instead of being worked for the extraction of sugar is often fermented and distilled. The juice is made slightly acid with sulphuric acid to prevent any viscous fermentation, and a small quantity of brewer's yeast is added. The temperature of the fermentation is from 20° to 22° C., and the process is usually complete in from twenty-four to thirty-six hours.

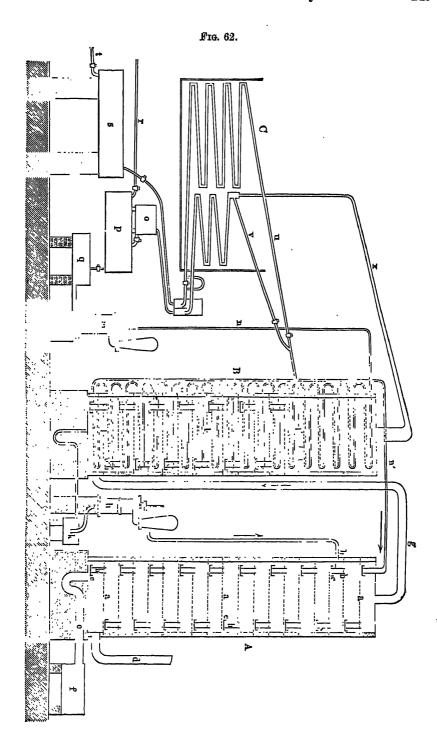
The use of the molasses obtained in the extraction of the raw sugar, whether from the sugar-beet or the sugar-cane, is, however, much more common. In France and Germany, where the beet-sugar molasses is produced in large quantities, the molasses originally marking 40° to 48° Beaumé is diluted to 8° or 10° Beaumé, and sulphuric acid of 66° is added to the amount of 1.5 per cent. of the molasses taken. This neutralizes the bases of the beet-molasses and inverts the cane-sugar present, bringing it into fermentable form. Brewer's yeast is then added, and the fermentation proceeds rapidly. The temperature ranges from 22° C., that usually chosen in France, where more dilute solutions are fermented, to 25° to 30° C. in Germany, where the concentration is usually as much as 12° B. Two hundredweight of molasses at 42° B. will furnish about six gallons of pure spirit.

In the West Indies, notably in Jamaica, the cane-sugar molasses is similarly utilized, but the procedure is somewhat different. In this case the addition of yeast is unnecessary, as the nitrogenous matters present suffice to start spontaneous fermentation. The best rum is that gotten from the molasses alone; a second grade is obtained from the skimmings

and "sweet-waters" which accumulate in the extraction of the sugar. To these is added some "dunder" (fermented wash, deprived by distillation of its alcohol and much concentrated by boiling), which acts as the ferment and starts the action. Molasses is then added in the proportion of six gallons to every hundred gallons of the fermenting liquid and the action allowed to go to completion. One hundred gallons of this mixture when distilled should yield twenty-five gallons of "low wines" or one gallon of proof rum for each gallon of molasses employed.

3. DISTILLATION OF THE FERMENTED MASH, OR ALCOHOLIC LIQUID.— Upon the construction of apparatus for the distilling from the fermented mash of the alcohol which it contains much skill and ingenuity have been displayed, and some of the later forms of stills and rectifying apparatus employed in large distilleries are wonderfully adapted for obtaining in a continuous operation the purest and strongest alcohol from the crude fermentation products. We may distinguish some five main classes of distilling apparatus, of which the minor varieties are too numerous to be specially enumerated. These classes are: first, simple stills with worm condenser heated by direct firing; second, simple stills with closed "washwarmer "; third, stills with rectifying "wash-warmer"; fourth, stills with "wash-warmer," rectifying and dephlegmator apparatus for intermittent working; and, fifth, similar forms of construction for continuous working. The first and simplest of these classes hardly needs any special description. The stills are usally of copper, flat-bottomed, and often of great size, especially in Irish and Scotch whiskey distilleries. It is obvious that their use involves a great waste of fuel. Therefore one of the earliest devices for economizing the heat of distillation consisted in interposing between the still and the refrigerating apparatus a "washwarmer," or vessel filled with the liquid ready for distillation. Through this vessel the pipe conveying the hot vapors to the refrigerator coil passed, and the vapors partly condensing there heated up the wash. which then went into the still quite hot. Dorn's apparatus, still somewhat used in smaller establishments in Germany, accomplished the same thing, and effected a partial rectification of the distillate by having interposed between the still and the refrigerator a vessel divided horizontally into two compartments by a diaphragm of copper. The upper and larger compartment served as a wash-warmer, and through it the tube conveying the vapors from the still passed into the lower compartment. where at first the distillate condensed. As the wash becomes warmed up this distillate gives off alcoholic vapors, which then pass on and are condensed in the worm, while the watery portion is allowed to flow back into the still by a side-connection. It is obvious that this rectifying action can be increased by the introduction of two or more such vessels between the still and the final condenser, and so a distillate much richer in alcohol be obtained.

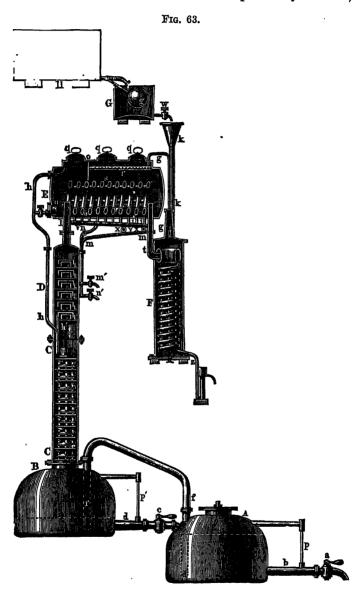
Another principle was now brought into play in effecting a fractional condensation, that of dephlegmation, or chilling the vapor coming off by contact with metallic diaphragms so that a portion of it, and of course the most watery is condensed and separated while the richly alcoholic



vapor passes on into the rectifier or condenser. Three types of these most elaborate apparatus may be briefly referred to: the Pistorius apparatus, used in Germany for the thick potato-mashes of that country. which is intermittent, the Coffey still, used in England and Scotland for the thinner worts from grain, and the column apparatus, first introduced by Savalle and improved by later inventors, which is used in France for distilling wines and in Germany to follow up the work of the Pistorius or similar apparatus. Both the Coffey still and the column apparatus are continuous in action. In the Pistorius apparatus, two boilers and a wash-warmer are used for the fresh mash, and are connected so that the vapors from the first boiler pass into the second boiler, heating it up and in time driving vapor from it, which then passes around the washwarmer and goes through several dephlegmators placed one above the other. In these the watery alcohol is continually being condensed and running back to the second boiler, while the uncondensed vapor which escapes from the top dephlegmator goes finally to the refrigerating apparatus. The Pistorius apparatus has been improved upon by Gall, Schwartz, and Siemens. The Coffey still, illustrated in Fig. 62, consists of two columns placed side by side, made of wood and lined with copper. The analyzer, A, is divided into twelve small compartments by four horizontal plates of copper, a, perforated with numerous holes and furnished with valves opening upwards. Dropping-pipes, b b, are also attached to each plate, the upper end of the pipe being an inch or two above the plate and the lower end dipping into a shallow pan, c, placed on the lower plate. The second column or rectifier, B, receives the spirituous vapors passing from the column A through the pipe g. This column is also divided into compartments like A, but there are fifteen instead of twelve. The ten lower diaphragms, l, are pierced with small holes and furnished with drop-pipes, while the upper five have only one large opening surrounded by a ring to prevent the finished spirit from returning. Between each of these compartments passes a bend of a long zigzag pipe, n n', one end of which is attached to the pump m, whilst the other end discharges the contents of the pipe into the top of the column A. as indicated by the arrow. The following is the working of the apparatus. In the first place, the fermented liquor or wash is pumped up by the pump m until the zigzag pipe is filled and the wort flows over the compartments a a a. Steam is then admitted into the compartments of the analyzer by the pipe d and heats the wash, which is deprived of all its alcohol by the time it reaches the bottom of the clyinder and flows off by e f as spent wash. The strong spirituous vapor passes through a to the rectifier, and at last through the worm c of the refrigerator into the receiver. The Coffey still is recognized as the best and most economical device for preparing a highly-concentrated spirit in a single operation. It is specially adapted for preparing from grain-mashes what is called "silent spirit," which is almost entirely destitute of flavor, and of a strength ranging from fifty-five to seventy over proof. It is not so well adapted for the distillation of malt whiskey as fire-heated stills, because the peculiar flavor of the whiskey depends upon the retention by the

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alcoholic distillate of the volatile oils produced in the mash, and the Coffey still separates the alcohol from these as well as other impurities. The forms of apparatus used in France for the distillation of wines are illustrated in that of Cellier-Blumenthal as improved by Derosne, shown



in Fig. 63. The alcoholic vapors from A pass into B, and thence into the rectifying column C, which contains a series of perforated metal cups over which wine from the wine-warmer, E, is trickling. The vapors thus enriched go through the upper rectifying column, D, and thence to the wine-warmer, E, which serves as a first condenser, and then to the cold



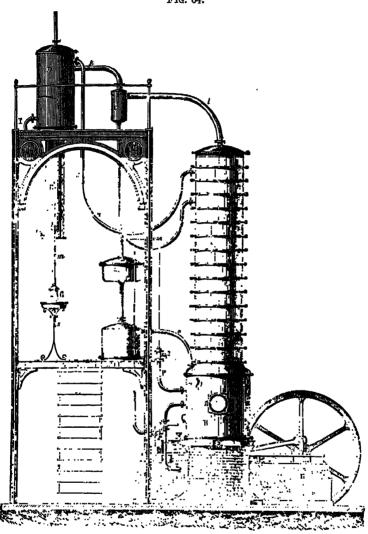


Fig. 65.

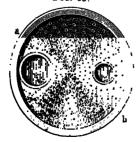


Fig. 66.



condenser, F, and so to the collecting vessel. After the operation is well under way the supply of wine can be introduced from H through G, k, and E, while the de-alcoholized liquid can be run off from the lower side of A.

Another form of still very largely used in France and Belgium, especially for thin mashes like molasses and beet-mash, is that of Savalle, illustrated in Fig. 64. It is a continuous-working apparatus. B is the still proper heated by steam-pipes, A is the rectifying column, C is for catching froth, D is a warm tube condenser and E the cold condenser. The elements which form the condensing and rectifying parts of the column A are shown in Figs. 65 and 66. The vapors rising pass through the holes of the perforated plates, on which rests a layer of condensed liquid which can only drain down through d into the cup c placed below it. From these cups it overflows upon the perforated plate and is again drained off by the next connecting tube, d. The rising vapors are therefore washed by the liquid upon each perforated plate.

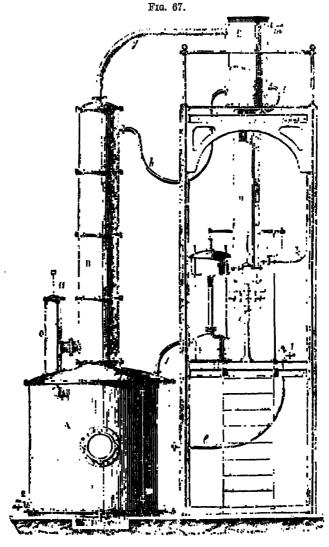
4. Rectifying and Purifying of the Distilled Spirit.—The products from the preliminary distillation from the fermented grain- or potato-mash are not at first sufficiently strong, but must be strengthened by rectifying. In England, the spirits obtained by the first distillation from grain-mash are generally called low wines, and have a specific gravity of about .975. By rectifying, or doubling, a crude milky spirit, abounding in oil, at first comes over, followed by clear spirit, which is then caught separately. When the alcoholic strength of the distilled liquid has considerably diminished, the remaining weak spirit that distils over, called faints, is caught separately and mixed with the low wines preparatory to another distillation. The rectifying is most rapidly and effectually done in the several forms of column apparatus, the best of which will yield a very pure alcohol in one or two operations.

An improved Savalle rectifying column as used generally in French and Belgian distilleries is shown in Fig. 67. It consists of a still, A. heated by closed steam-coils, a rectifying column, B, two tubular condensers, C and D, from the upper of which any condensed vapors flow back into the rectifying column as "low wines," while the lower condenser takes the more volatile product and passes it on as high-grade alcohol to the receiving-vessel, F.

The purifying of raw spirit, notably that from grain and potatoes, from what is called fusel oil (propyl, isobutyl, and amyl alcohols) is also a matter of great importance if the spirit is to be used as the basis of any manufactured liquors. This fusel oil sticks persistently to the alcoholic distillates, and alcohol rectified until it reaches a strength of ninety-five or ninety-six per cent. by volume contains fusel oil. Some acetaldehyde also remains dissolved in the alcohol, giving the raw spirit a bitter taste. The rectifier's method is to dilute the alcohol with water until it is about fifty per cent. strength, by which means the fusel oil separates out insoluble in the dilute spirit, and then to filter through wood charcoal. Another method which has been experimented upon on a large scale, known as the Bang and Ruffin process, is to shake up the diluted spirit

with petroleum oils, which have the power of absorbing the fusel oil and so withdrawing it from the dilute alcohol.

In this country the storage of the grain spirit in charred oaken barrels in warm rooms is extensively practised as a method of improving



the quality of the spirit. It was supposed that the fusel oil disappeared during this storage, but Crampton \* has shown that it does not and is merely masked by the empyreumatic extractive matter taken up from the wood. Esters, however, are formed and the rawness disappears.

5. MANUFACTURE OF ALCOHOLIC BEVERAGES FROM RECTIFIED SPIRIT.—Much of the rectified spirit, from whatever source derived, is used in

<sup>\*</sup> Journ. Amer. Chem. Soc., Jan., 1908, p. 98.

connection with the manufacture of wines for fortifying them and in arresting fermentation at any desired stage. The so-called "silent spirit" made in England by the use of the Coffey still from grain-wort is largely utilized in the manufacture of factitious brandies and wines, and the same thing applies to the spirit manufactured in France from beet-roots and beet-root molasses, where it is made to supply the deficiencies in the wine and Cognac production. The composition of many of these factitious or imitation liquors will be spoken of in the next section in enumerating the products of this industry.

#### III. Products.

1. Rectified and Proof Spirit.—'Rectified spirit' is the name often given to the most concentrated alcohol producible by ordinary distillation. The British Pharmacopæia describes rectified spirit as containing ninety per cent. by volume real alcohol and having a specific gravity of .834. The United States Pharmacopæia under the name "alcohol" simply calls for a spirit containing 94.9 per cent. by volume of real alcohol and having a specific gravity of .816 at 60° F. The "spirit" of the German Pharmacopæia has a specific gravity of .830 to .834, and hence corresponds more nearly to the British "rectified spirit."

"Proof spirit" is a term in constant use in England for the purposes of excise, and its strength was defined by act of Parliament to be such that at 51° F. (10° C.) thirteen volumes shall weigh the same as twelve volumes of distilled water. The "proof spirit" so made will have a specific gravity of .91984 at 15.5° C. (60° F.) and contain, according to Fownes, 49.24 per cent. by weight of alcohol and 50.76 per cent. of water. Spirits weaker than proof are described as U. P. (under proof), stronger than proof as O. P. (over proof); thus, a spirit of fifty U. P. means fifty water and fifty proof spirit, while fifty O. P. means that the alcohol is of such strength that to every one hundred of the spirit fifty of water would have to be added to reduce it to proof strength. Tables are in use which give for alcohol of a given specific gravity at 15.5° C. (60° F.) the corresponding percentage by weight, percentage by volume, and percentage of proof spirit contained. (See Wynter Blyth, Foods, Composition and Analysis, 5th ed., p. 380.)

2. Alcoholic Beverages made by Direct Distillation of the Fermentation Products.—Arrack.—Any alcoholic liquor is called "arrack" in the East, but arrack proper is a liquor distilled either from toddy, the fermented juice of the cocoa-nut palm, or from malted rice. The arrack from Goa and Columbo is considered the best, and is made from toddy alone. This latter is gotten by the incision of the palm, and is collected in pots hung to the tree under the cuts. It is then fermented and distilled. In preparing the other variety, as carried out in Batavia and Jamaica, the rice is covered with water and allowed to germinate, dried at a temperature of 59° F., which arrests germination, and then a wort is made from the malted rice in the same manner as from malted grain, which is afterwards distilled. The commonest pariah arrack of India is

generally narcotic, very intoxicating, and unwholesome. It is prepared from coarse jaggery sugar, spoilt toddy, refuse rice, etc., and rendered more intoxicating by the addition of hemp leaves, poppy-heads, juice of stramonium, and similar deleterious substances.

Brandy in its purest form (Cognac) is the direct product of the distillation of French wines. Its peculiar flavor and aroma are due to the presence of ethyl pelargonate (cenanthic ether). The better qualities of Cognac are distilled from white wines, the inferior varieties from the dark-red Spanish and Portuguese wines or from the marc or refuse of the wine-press, and called eau de vie de marc. A great deal is also entirely factitious, being mixtures of grain spirit and water to which different coloring and aromatic substances have been added. When first distilled, brandy, like other spirituous liquors, is colorless, when it is known as white brandy, and continues so if kept in glass- or stone-ware, but if stored in oak casks, as is usually the case, it gradually acquires a vellowish tint from the wood, and it is then termed pale brandy. The still deeper color which it frequently possesses is given it by the addition of caramel-color, which was originally designed to simulate the appearance of an old brandy long stored in casks. The coloring matter is also sometimes prepared from catechu and similar astringent and aromatic substances.

Numerous recipes for factitious brandies are furnished for the use of rectifiers in making up imitations of Cognac. Two such recipes are given:

No. 1.—Powdered catechu, 100 grammes; sassafras-wood, 10 grammes; balsam of tolu, 10 grammes; vanilla, 5 grammes; essence of bitter almonds, 1 gramme; well-flavored alcohol (at 85°), 1 litre.

No. 2.—Malt spirit (17 U. P.), 100 gallons; nitrous ether, 2 quarts; ground cassia-buds, 4 ounces; bitter almond meal, 5 ounces; sliced orrisroot, 6 ounces; cloves in powder, 1 ounce; capsicum, 1½ ounces; good vinegar, 3 gallons; brandy-coloring, 3 pints; powdered catechu, 2 pounds; full-flavored Jamaica rum, 2 gallons. Mix in an empty Cognac-cask and macerate for a fortnight, with occasional stirring. Produces 106 gallons at 21 or 22 U. P.

Kirschwasser is a spirituous liquor obtained in the Black Forest and in Switzerland by the distillation of cherries. These are picked free from the stalks and only the sound fruit taken. They are crushed for the extraction of the juice, and a portion of the cherry-stones are then separately crushed so as to bruise the kernels and returned to the juice. These bruised kernels impart the almond flavor to the product and give to it a small quantity of prussic acid (.15 gramme per litre in good kirsch and more in inferior kinds). After fermentation the liquor is drawn off and distilled by steam. The kirsch is colorless, of agreeable odor and flavor, which improves by keeping, and equal in strength to the strongest spirit.

Rum is a spirit obtained in the West Indies, notably in Jamaica, Martinique, and Guadeloupe, from the molasses of the sugar-cane by fermentation and distillation. The process of fermentation of the molasses

as carried out in Jamaica has already been described. When new, rum is white and transparent, and has when freshly distilled an unpleasant odor, due to oils contained. These are got rid of by treatment with charcoal and lime. It owes its characteristic flavor to butyric ether, which compound is also prepared artificially on a large scale, and as rum essence is used with "silent spirit" to make a factitious rum. Rum is always colored artificially with caramel-color.

Whiskey is the spirit obtained from the fermented wort of corn, rye, and barley, either raw or malted. In Scotland and Ireland, malted barley, pure or mixed with other grain, is chiefly used; in the preparation of the Bourbon whiskey of Kentucky partially-malted corn and rye are taken, while for the Monongahela whiskey of Western Pennsylvania only rye (with ten per cent. of malt) is used.

The difference between the Irish and the Scotch whiskeys lies mainly in the fact that the latter is distilled from barley malt dried by peat fuel, giving a characteristic smoky flavor to the spirit, while the malt of the Irish whiskey is destitute of this flavor. Both are in general pot-still whiskies, while the product of the Coffey still with less flavor is used for blending. The Irish "poteen" whiskey, however, has the smoky flavor and this is imitated by the addition of one or two drops of creosote to the gallon of spirits.

3. Alcoholic Beverages made from Grain Spirit by Distillation under Special Conditions.—Gin is common grain spirit distilled and aromatized with juniper-berries, either when the "low wines" are concentrated or later, using full-strength spirit. The proportion employed is variable, depending upon the nature of the spirit; usually one kilogramme of berries is enough to flavor one hectolitre of raw grain spirit. The finest gin, known as "Hollands," is made in the distilleries of Schiedam, whence also the name "Schiedam Schnapps." Strassburg turpentine, oil of fennel, coriander and cardamom seeds are frequently substituted either wholly or in part for the juniper-berries, particularly in the English-made gin. The quality and healthfulness of the gin depend largely upon the purity of the spirit used in the distillation, whether raw or rectified.

It is obvious that many factitious brandies belong also in this class, being made by distillation of mixtures of which grain spirit is the basis and not by distillation of wine. These have already been described.

4. LIQUEURS AND CORDIALS.—Liqueurs is the name now given to such spirituous drinks as are obtained by mixing various aromatic substances, such as anise, absinthe, essence of orange-peel, etc., with brandy or alcohol. Most are obtained by steeping in pure brandy or spirit different fruits or aromatic herbs and submitting the resulting liquid to distillation. They are then colored, and are usually sweetened with sugar. The best known of them, absinthe, contains a characteristic ingredient, oil of wormwood, to which its deleterious effects on the nervous system are supposed to be due. At the same time the amount of total essential oils held dissolved in the strongly alcoholic liquid is such that when diluted with water the solution becomes milky and turbid.

Among the liqueurs may be enumerated Absinthe (consumed chiefly in Paris), Anisette (made in the south of France), Chartreuse (made by the monks of the Grande Chartreuse Monastery near Grenoble), Curaçoa (originally made in Holland of Curaçoa oranges), Maraschino (made in Italy of Dalmatian cherries), Ratafia (made in France from a great variety of fruits), and Usquebaugh (a strong cordial made in Ireland. It furnishes the name from which the word whiskey is derived).

The composition of the several alcoholic liquors enumerated cannot be given in great detail, as their differences depend so largely upon the flavoring and aromatic ethers and essential oils, which are present in very minute quantities. Their general differences in alcoholic strength and the extract and ash of several are, however, given on the authority of König:\*

	Alcohol by volume.	Alcohol by weight.		Alcohol by volume.	Alcohol by weight.
Russian Dobry wutky Scotch whiskey Irish whiskey English whiskey American whiskey	62.0 50.3 49.9 49.4 60.0	54.2 42.8 42.3 41.9 52.2	Gin Ordinary German schnapps Rum	47.8 45.0 49.7 55.0	40.3 87.9 42.2 47.3

## And in one hundred cubic centimetres of the following:

	Specific gravity.	Alcohol by volume.	Alcohol by weight.	Extract.	Ash.
Arrack	0.9158	60.5	52.7	0.082	0.024
	0.8987	69.5	61.7	0.645	0.009
	0.9378	51.4	84.7	1.260	0.059

The composition of some of the well-known liqueurs is also given on the same authority: †

	Specific gravity.	Alcohol by volume.	Alcohol by weight,	Extract.	Cane- sugar.	Other ex- tractions.	Ash.
Absinthe Bonekamp of Maag bitters Benedictine bitters Ginger Orème de menthe Anisette of Bordeaux Curaçoa Kümmel liqueur Peppermint liqueur Swedish punch	0.9116 0.9426 1.0709 1.0481 1.0447 1.0847 1.0800 1.0830 1.1429 1.1080	58.93 50.0 52.0 47.5 48.0 42.0 55.0 88.9 84.5 26.3	42.5 44.4 40.2 40.7 35.2 47.3 28.0 28.6 21.6	0.18‡ 2.05 86.00 27.79 28.28 84.82 28 60 82.02 48.25 86.61	32.57 25.92 27.63 34.44 28.50 31.18 47.35	0.82 	0.106 0.043 0.141 0.068 0.040 0.040 0.058 0.068

<sup>\*</sup> König, Nahrungs- und Genussmittel, 3te Auf., vol. i, p. 992.

<sup>†</sup> Ibid., p. 997.

<sup>‡</sup>Oil of wormwood.

5. Side-products.—The distiller's residue (Schlempe, vinasse) form a side-product of considerable value as a cattle food because of its composition. It is especially rich in protein matter, fat, and non-nitroger ous extractive, or earbohydrates. The residues from the beet- and can molasses distillation, moreover, yield an ash very rich in potash salts, s that they constitute, especially in France, a very important source c potashes. The constituents of several of these distillery residues in the moist state are here given on the authority of König:\*

	Water.	Fat.	Nitro- genous matter.	Non-nitro- genous extract.	Cellulose.	Ash.
Rye-mash residues (ten analyses) Potato-mash residues (six analyses) Molassos residues	93.48 95.10 91.86	0.22 0.17	1.40 1.17 2.04	4.05 2.17 4.56	0.52 0.92	0.88 0.47 1.54

Two complete analyses of distillery residues dried by centrifugatin and heating in kilns are given on the authority of Rosenbaum: †

Water 11.62	7.83
Ash 6.50	16.40
Crude proteid matter 21.44	23.08
Crude fibre 10.54	8.60
Non-nitrogenous extractives 38.96	40.54
Crude fat 11.44	3.55
100.00	100.00

Of these constituents the following were assimilable as food:

Albuminoids	17.20	18.50
Carbohydrates		39.40
Fat		2.85

## IV. Analytical Tests and Methods.

The most important determination in this class of beverages is the alcoholic strength. In the case of rectified or proof spirit, a simp specific gravity determination is all that is necessary, and then the percentage strength can be found from the alcohol tables that have been prepared. The determination should be made at 15.5° C. (60° F.), if at another temperature, a correction in the reading must be made By multiplying the number of degrees above or below 15° by .4 are adding the product to the percentage given by the table when the temperature is lower than 15°, or deducting it when the temperature above, we get a correct result. In freshly-distilled and colorless whiskey and brandies, in which the amount of extract is trifling, the alcohol

<sup>\*</sup> König, Nahrungs- und Genussmittel, 2te Auf., vol. ii, p. 468.

<sup>†</sup> Jahresber. der Chem. Technol., 1887, p. 1058.

percentage can also be determined with sufficient accuracy by the specific gravity method. In such liquors as contain more extractive matter, like rum and the liqueurs and cordials, the alcohol must first be distilled off, and then made up to original volume with distilled water, as described on p. 235.

The detection and determination of fusel oil, which is a persistent impurity in potato and grain spirit, is one of the most important tests to be made. To detect it, the greater part of the alcohol is distilled off at as low a temperature as possible, the residual liquid mixed with an equal amount of ether and well shaken. The ethereal layer is then separated and allowed to evaporate spontaneously, when amyl alcohol, if present, will be recognized in the residue by its smell and chemical characters. Petroleum-ether may be advantageously substituted for the ether in this test.

Two quantitative methods are now in use, the Roese method in which the increase in volume of a measured amount of chloroform when shaken with a distillate from the sample in question is compared with that obtained in a blank experiment with fusel-free alcohol, and the Allen-Marquandt method in which the fusel oil extracted with a solvent (preferably carbon tetrachloride) is oxidized by bichromate of potash and sulphuric acid, the volatile acids produced distilled off and titrated with one-tenth normal sodium hydroxide solution. For full working directions for the use of these processes see "Official and Provisional Methods of Analysis," Bulletin No. 107 (Revised) Bureau of Chemistry, Department of Agriculture.

Caramel (burnt sugar) is used for coloring and flavoring spirits, and may be detected by the Crampton and Simons test. Evaporate fifty cubic centimetres of the sample nearly to dryness on the water-bath, wash into a fifty cubic centimetre flask, add twenty-five cubic centimetres of absolute alcohol, cool to a definite temperature and dilute to mark with water. Transfer twenty-five cubic centimetres to an apparatus such as is used in the Roese fusel oil determination, add ether (fifty cubic centimetres) and shake at intervals for half an hour and allow to settle. After withdrawing the water, the aqueous layer is compared with twenty-five cubic centimetres of the solution which have not been treated with ether. The amount of color removed is expressed on the percentage basis.

The Amthor test, as modified by Lasché, is based upon the action of paraldehyde solution upon a sample of the liquor. A permanent turbidity after ten minutes indicates caramel.

Tannin is often present in brandy and whiskey, being chiefly extracted from the casks used in storing. Sometimes, as in factitious brandies, it is purposely added in the form of tincture of oak-bark. It may be detected by the darkening produced on adding ferric chloride to the spirit, and any reaction thus obtained may be confirmed by boiling off the alcohol from another portion of the spirit and adding solution of gelatine to the residual liquid, when a precipitate will be produced if tannin be present.

#### E. BREAD-MAKING.

Bread-making as ordinarily conducted is to be classed as one of the fermentation industries, as the swelling of the dough which must precede the baking is generally accomplished by the aid of the alcoholic fermentation brought about by the addition of "leaven" or yeast. For every kilogramme of bread, on the average, 2.5 grammes of alcohol and 2.7 grammes of carbon dioxide gas are produced. Both are lost in the baking, but the carbon dioxide gas when first generated is caught in the thick and viscid dough and causes it to swell up and become spongy in structure. This not only gives to the bread when baked a porous and cellular structure, but allows the chemical changes to take place throughout its entire substance, whereby it is made more readily digestible.

As the only effective result of the alcoholic fermentation is performed by the carbon dioxide, of course the addition of chemical mixtures liberating carbon dioxide gas in the dough may be made to obviate the necessity of using leaven or yeast, and similarly aerated breads may be made by simply forcing carbon dioxide under pressure into the dough.

A few varieties of bread are made from dough, baked without any aeration either natural or artificial, such as hard crackers, the unleavened bread of the Jews, the Scotch oat-cake, and the corn-cake of the Southern States. These exceptions are of relatively minor importance, and by far the largest amount of bread is prepared by the aid of a fermentation process.

## I. Raw Materials.

1. FLOUR.—This may be from either wheat, rye, barley, oats, maize, —Indian corn,—or rice, although wheat flour is used in far the largest amount.

The average composition of the several cereals has already been given. (See page 186.) Wheat flour contains the following substances: starch, dextrine, cellulose, sugar, albumen, gliadin, or gluten, mucin, fibrin, cerealin, fat, mineral matters, and water. The first four are carbohydrates, or non-nitrogenous substances, and they form nearly three-fourths of the entire weight of the flour. The nitrogenous matter consists of at least five principles, three of which, gluten (or gliadin), mucin (or mucedin), and fibrin, constitute the bulk of the material known as crude gluten, which is the substance left when flour is kneaded with water and afterwards washed to remove the starch and any soluble substance. The remaining two nitrogenous principles, albumen and cerealin, are soluble in water, and are carried away with the starch in the process of washing. Crude gluten possesses a peculiar adhesiveness, arising from the presence of gliadin, which is a highly tenacious body, and which is not present in the same form in other cereal flours. It is this adhesive property which gliadin imparts to gluten that renders wheaten flour so well adapted for bread-making purposes.

The vegetable albumen mentioned above as soluble in cold water is accompanied also by small amounts of legumin, or vegetable casein,

which is also soluble in water. The cerealin is a soluble nitrogenized ferment occurring especially in the husk or bran of wheat and other cereals. It has a powerful fermentative action on starch, rapidly converting it into dextrine and other soluble bodies. The presence of cerealin in bran renders "whole meal" unsuitable for making bread by fermentation with yeast, though it can be used with baking-powders, and "aerated bread" can be made from it. The cerealin acts like malt extract, causing a too rapid conversion of the starch into dextrine and sugar, and hence, although the bran is rich in nitrogenous food constituents and salts like phosphates, it is ordinarily separated from the flour. The difference in the composition of the several parts of the wheat-grain is seen in the following table given by Church: \*

	Fı	ne White	Coa	RSE WHE	AT BRAN	7.	
	In 100 parts.				In	1 pound	l <b>.</b>
Water Fibrin, etc. Starch, etc. Fat Cellulose Mineral matter	13.0 10.5 74.3 0.8 0.7 0.7	2 ounce 1 " 11 " 0 " 0 "	8 35 grains. 297 '' 888 '' 57 '' 49 ''	14.0 15.0 44.0 4.0 17.0 6.0	2 ounc 2 " 7 " 0 " 2 " 0 "	es 105 g 175 17 280 316 422	rains.

Of course, milling processes have to be specially adapted to the separation of these quite different parts of the wheat-grain, the white flour free from bran being sought. By the old-fashioned "low-milling" process, or grinding between stones placed very close together and bolting, it was impossible to obtain a flour entirely free from contamination. The advance to "high-milling" with stones far apart, allowing the middlings which were produced to be purified before grinding to flour, was a step which made it possible to make from winter wheat an excellent and pure flour. When, however, spring wheat with its hard and brittle outer coats became important commercially, it was necessary to resort to the roller methods of milling, which, in conjunction with peculiar purifying machinery, would furnish a flour free from all undesirable impurities. This latter process has now almost universally replaced the other in the newer mills.

While most of the other cereals before mentioned may be found occasionally in admixture with wheat flour, very few are used alone as substitutes for it. Rye flour is probably the only one. It makes a dark-colored, heavy and sourish bread, which, however, keeps moist a long time. It is much used in Germany and Northern Europe under the name of "black bread." A more palatable bread may be made from a mixture of two parts wheat flour and one part rye flour. This latter flour contains a slightly larger amount of fat and of mineral matter than wheat flour. It is never so white as wheat flour and the gluten has very little adhesive character. Ritthausen states that the gluten of rye flour con-

<sup>\*</sup> A. H. Church, Foods, etc., South Kensington Hand-book, pp. 63 and 64.

sists chiefly of mucin (mucedin) and vegetable casein, and that gliadin is absent entirely.

2. Yeast, or Ferment.—The yeast is at present almost always added, either as brewer's yeast or compressed yeast. In former times (and to a considerable extent still in France) wheat bread was made by the use of leaven, which consists of a portion of dough left over from a previous baking, charged with the ferment and in part changed by its action. The leaven is originally gotten by allowing flour and water to start into spontaneous fermentation, the nitrogenous matters becoming soluble and attacking the starch and sugar. The leaven tends, however, to continue its decomposition and to pass from the alcoholic into the lactic fermentation. Hence, if the leaven is in the proper stage of decomposition, it will induce the alcoholic fermentation and generate carbon dioxide gas, raising the dough; if it be, however, in a more advanced state of decomposition, lactic fermentation will be induced and the bread will not rise. but become heavy and sour. In domestic practice, to avoid this latter result, saleratus (bicarbonate of potash or soda) is added to the dough. This neutralizes the lactic acid as fast as formed, and at the same time liberates carbon dioxide gas to inflate the dough. An excess of this salt, however, makes the bread alkaline to the taste and yellow in color.

The black rye bread of Germany is also made with the aid of a leaven known as "sour dough." In this both the alcoholic and the lactic fermentations are in progress, the latter, however, preponderating. Four parts of such sour dough are used for one hundred parts of flour.

The brewer's yeast for bread-raising purposes must be a fresh and vigorous yeast-growth, as its value here depends largely upon the energy of the fermentation set up and the amount of gas given off. Its appearance and characters have been described before. (See p. 207.) Unless of the best quality, compressed yeast is to be preferred because of its reliability. The manufacture of this latter is carried out chiefly in connection with the spirit distilleries. At the time when the fermentation is most energetic, the yeast is skimmed off the surface and conveyed by wooden shoots to steam sieves, by which the husks are eliminated, the strained liquid passing on to the settling cisterns. When settled the surface liquid is drained off and sent for distilling purposes, and the yeasty sediment mixed with starch and put into the filter-presses, which squeeze out all the liquid, leaving a dough-like paste, which, when sufficiently dry, is packed into bags and packets and is ready for distribution. Yeast from its peculiar slimy nature cannot be pressed well, hence the addition of starch, which permits the removal of more of the liquid from the yeast. Absolutely pure yeasts do not keep so well as the same yeasts with an addition of from five to ten per cent. of starch. In highclass yeasts the quantity added is about five or six per cent.; it is often added in quantity beyond this as an adulterant. A good sample of compressed yeast has the following characteristics: It should be only very slightly moist, not sloppy to the touch; the color should be a creamy white; when broken it should show a fine fracture; when placed upon the tongue it should melt readily in the mouth; it should have an odor of apples, not like that of cheese; neither should it have an acid taste or odor. Any cheesy odor shows that the yeast is stale and that incipient decomposition has set in.

3. Baking Powders .- To obviate the necessity of using yeast and waiting until the dough should rise sufficiently under the influence of fermentation, it was early sought to supply the necessary carbon dioxide to the dough by chemical reactions. The earliest proposal was that of Liebig to use sodium bicarbonate and hydrochloric acid, which should evolve carbon dioxide and leave sodium chloride (common salt) in the dough. Next was proposed sodium bicarbonate and tartaric acid, or acid potassium tartrate (cream of tartar). More generally satisfactory than either of these was acid calcium phosphate (either alone or with acid magnesium phosphate), which with bicarbonate of soda formed Horsford's baking-powder. More objectionable was the introduction of alum with the sodium bicarbonate. Most of these baking-powder mixtures, then, have starch or flour added as "filling," and in amount varying from twenty to sixty per cent. Sesquicarbonate of ammonia is also used in many of the mixtures, replacing part of the bicarbonate of soda. Self-raising flours have these baking-powders already added to the flour in such proportions as will insure a spongy dough upon the simple addition of water and kneading into loaves.

### II. Processes of Manufacture.

1. THE MIXING OF THE DOUGH AND ITS FERMENTATION.—The mixing of the flour with water is not only for the purpose of bringing into solution the dextrine, the sugar, and the soluble albuminoids, and of allowing these latter as peptones to act upon the insoluble consituents of the flour, such as the gluten, but also to penetrate and soften the starchy material.

The yeast may be added directly along with the water to some of the flour to prepare a "sponge," from which the whole batch of dough is afterwards made, or a "ferment" may be made from the yeast with potatoes, which then is used to prepare the "sponge." In the latter case, potatoes are boiled and mashed with water into a moderately thin liquor, to which the yeast is added, and the fermentation is allowed to proceed for some time. In either case, whether the yeast is used direct or a potato ferment is first made, it is worked up with a portion of the flour into a slack dough, which constitutes the sponge, and is set to rise in a warm place. When the sponge has risen sufficiently the remainder of the flour is worked in with sufficient water to which some salt has been added, and the dough is made, kneaded, allowed to stand again to rise, and then prepared for baking.

The use of potato ferment is based upon the belief that the yeast-cells are strengthened by the soluble nitrogenous matter of the potato, which acts as a yeast stimulant and enables a smaller quantity of yeast to hydrolyze a larger amount of starch. The yeast-cells then act very rapidly upon the glucose so produced and develop the alcoholic fermentation. The albuminoids of the flour are also softened and partially peptonized, and these changed albuminoids in turn assist in the hydrolysis of the starch.

2. Baking.—For baking, the oven should have a temperature of 400° to 450° F. (200° to 230° C.). Before putting the loaves in, they are often wetted on the surface so as to assist in the prompt formation of a crust that shall prevent the dough from expanding too rapidly. The heat expands the gases throughout the loaf and so swells it and vaporizes a portion of the moisture. The action of the heat and steam soon converts the starch on the surface of the loaf into dextrine and maltose, and these at the high temperature are slighly caramelized, thus giving the crust its brownish color. At the temperature of the interior of the loaf (212° F. or slightly above) the starch-cells will have burst, the coagulable albuminoids will have been coagulated, and their diastatic power entirely destroyed.

Steam is often injected into the oven during the baking. The effect is to produce a glazed surface on the outside of the crust. It not only dextrinizes and glazes the crust, but keeps the interior of the loaf moist by preventing too rapid evaporation. Of course, in perfectly tight ovens the steam resulting from the evaporation of the moisture of the bread is kept in, and soon acts in the same manner though in a lesser degree.

One hundred kilogrammes of flour will yield, according to its quality, from one hundred and twenty-five to one hundred and thirty-five kilos. of bread.

3. Use of Chemicals Foreign to the Bread.—Both alum and sulphate of copper (and notably the former) have been used in baking bread from inferior or unsound flours in order to improve the appearance of the bread. This form of adulteration is rarely practised at present. Much more important in recent years is the practice of bleaching flour with nitrogen peroxide. If not used in excess this promptly whitens the gray or slightly yellowish flour and increases the whiteness of the bread baked from the same. In the Alsop process most generally employed the nitrogen peroxide is formed by a flaming electric discharge which causes nitrogen and oxygen of the air to combine. Other processes use chlorine or bromine or nitrosyl chloride.

Liebig suggested the use of lime-water as a means of retarding too rapid decomposition of the starch during the fermentation of breadmaking. The bread made with the proper amount of lime-water is said by Jago\* to be more spongy in texture, pleasant in taste, and quite free from sourness. In the bread the lime exists as calcium carbonate, but in such quantities as to be perfectly harmless.

## III. Products.

1. Bread.—The nature of the change which the flour undergoes in the bread-baking process has already been indicated in part. The composition of the finished bread can now be noted. A loaf of wheaten bread consists of two parts, the *crumb* and the *crust*, which differ somewhat in both physical and chemical character. The crumb is white in color, more or less vesicular in structure, soft when fresh, and of agreeable taste and sweet odor; the crust is harder, more easily broken, of a chest-

nut-brown color, and nearly destitute of all porous character, is sweeter in taste, because of the greater change of the starch into dextrine and maltose. The chemical differences between well-known forms of bread are shown in the following analyses from the U. S. Bureau of Chemistry, Bulletin 13, Part 9:

	Number of analyses.	Moisture.	Proteids, N x 6.25.	Proteids, N x 5.70.	Ether extract.
Vienna bread	10	38.71	8 87	8.09	1.06
	2	33.02	7.94	7.24	1.95
	9	34.80	8.93	8.15	2.03
	7	33.42	8.63	7.88	0.66
	9	34.41	7.60	6.93	1.48
	48	7.13	10.34	9.43	8.67
	11	27.98	8.20	7.48	3.41

	Crude fibre.	Salt.	Ash.	Carbohy- drates, excluding fibre.	Calculated calories of com- bustion.
Vienna bread	0.62	0.57	1.19	53.72	4435
	0.24	0.56	1.05	56.75	4467
	1.13	0.69	1.59	53.40	4473
	0.62	1.00	1.84	56.21	4338
	0.30	0.49	1.00	56.18	4429
	0.47	0.99	1.57	73.17	4755
	0.60	0.69	1.31	59.82	4538

The differences between wheat bread made by the usual fermentation process and wheat bread aerated by carbon dioxide under pressure (Dauglish system) are shown also in the following analyses by Dr. Bell:\*

	AERATED BREAD.				Home-made Bread.				
CONSTITUENTS OF THE BREAD REDUCED TO DRY STATE.	Tin loaf.		Cob loaf (Paris bread).		Tin loaf.		Cob loaf (Paris bread).		
·	Crumb.	Crust.	Crumb.	Crust.	Crumb.	Crust.	Crumb.	Crust.	
Starch, dextrine, cellulose, etc. Maltose Nitrogenous matter, insolu-	78.93 6 40	78.96 5.61	82.75 4.66	82.82 3.94	78.12 6.87	77.62 6.68	82.05 4.85	83.42 4.11	
ble in alcohol	10.80	11.28	8.58	9.09	11.65	11.17	10.59	8.68	
alcohol	1.96 0.18 2.23	1.75 0.16 2.24		1.85 0.17 2.13	1.74 0.22 1.40	2.00 1.22 1.31	1.28 0.15 1.08	2.87 0.89 1.03	
Percentage of moisture in bread when new	44.09	19.19	41.52	16.48	42.02	22,92	41.98	20.02	

<sup>\*</sup> Analyses and Adulteration of Foods, p. 131.

2. Crackers and Hard Biscuit are made from a dough composed of flour and water, with the addition in special cases of a great variety of sweetening and flavoring ingredients, such as milk, eggs, sugar, butter or lard, spices, and flavoring essences. The dough prepared in large masses is passed between rollers, and from the sheet of dough so obtained by other machines are cut out the various forms desired. Sheets or trays of these dough-forms pass by automatic machinery into and through long ovens at a regulated rate of speed, which can be so controlled as to give them exactly the requisite exposure to the heat needed for baking.

## IV. Analytical Tests and Methods

1. FOR THE FLOUR.—The moisture is determined by drying five grammes of the flour in a water-oven until constant weight is obtained.

The starch is estimated from the amount of glucose which is produced from it by the action of dilute acid. Two grammes of the flour are boiled in a flask with inverted condenser for several hours with some twenty cubic centimetres of sulphuric acid suitably diluted. When the conversion of the starch is completed the solution is neutralized with soda, made up to definite volume with water, and the glucose determined with Fehling's solution either gravimetrically or volumetrically, as described under glucose. (See p. 175.) After deduction of the sugar found in a previous test to be contained in the sample, the difference is the amount produced from the starch, together with a small quantity from the dextrine and traces of fibre. One hundred parts of glucose correspond to ninety of the starch.

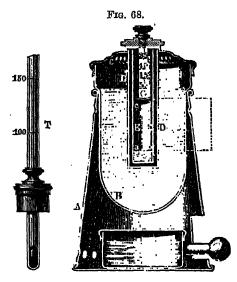
To determine the *cellulose*, a weighed quantity of the flour is boiled with rather dilute sulphuric acid for ten minutes to dissolve the starch. A large quantity of water is then added, and the undissolved part allowed to settle. The residue is thrown upon a filter, well washed with boiling water, and then digested with dilute potash solution to dissolve the albuminous matter. It is then washed upon a tared filter, dried, and weighed. It is now incinerated and the ash determined. This subtracted from the weight of material on the tared filter gives the cellulose or fibre.

To determine the *sugar*, ten grammes of the flour or powdered grain are repeatedly digested in alcohol of seventy per cent. and the filtrate made up to a bulk of three hundred cubic centimetres. This solution is first tested directly for glucose, but generally with negative results. A known portion of the filtrate is then boiled for four minutes with five cubic centimetres of normal sulphuric acid, neutralized with soda and tested with Fehling's solution, and the sugar present reckoned as cane is calculated from the result.

The total nitrogenous compounds, and the portions soluble or insoluble in alcohol, are generally determined. The total nitrogen is determined by the Gunning or Kjeldahl method and the nitrogen figure multiplied by 5.70 for wheat flour. For the alcohol soluble proteid ten grammes of the flour are completely exhausted with eighty per cent. alcohol at a temperature of 140° F. (60° C.) and an aliquot portion of

the total filtrate evaporated to dryness and weighed. A known quantity of this residue is then analyzed for nitrogen by the Kjeldahl or Gunning process, using the same factor 5.70 as before. The flour left after treatment with alcohol is dried, and a weighed portion analyzed for nitrogen and similarly calculated for albuminoids (albumen and fibrin).

The gluten is best determined as recommended by Wanklyn and Cooper.\* Ten grammes of the flour are mixed on a porcelain plate with four cubic centimetres of water so as to form a compact dough. This is placed in a conical test-glass or measure, fifty cubic centimetres of water added, and the dough manipulated with a spatula so as to free it from starch. The water is decanted off, a fresh quantity added, and the kneading continued until the water remains colorless. The gluten mass



is then removed, kneaded in a little ether, and spread out in a thin layer on a platinum dish, where it is dried by the aid of a water-oven until the weight is constant. The crude gluten contains ash equal to about .3 per cent. of the flour and fat equivalent to 1.00 of the flour.

An examination of the crude gluten as to its power of distending under the influence of heat is often made as a means of judging of the value of a flour for bread-making. This is done by the aid of the aleurometer of Boland, shown in Fig. 68. Some thirty grammes of the flour are kneaded as just described, and seven grammes of

the freshly-separated crude gluten obtained is placed in the inner vessel as shown at a b. In the mean time, while the gluten is being prepared, the tube D is heated by means of an oil-bath until the thermometer T, which is at first sunk in the tube D, registers 150° C. The thermometer is then withdrawn, and the aleurometer E, containing the gluten, put in its place. The spirit lamp under the oil-bath is allowed to burn for ten minutes longer and then extinguished. The piston G is graduated so that when pushed down it registers 25°. When the gluten swells and fills the space from a b to c d it touches the bottom of the piston and is at 25°. If it continues to swell the reading may be 30° or 35°, as shown on the scale when the piston is pushed up. If the gluten does not indicate at least 25° on the aleurometer it may be considered unfit for breadmaking. A similar instrument, termed an aleuroscope, has been invented by Sellnick.

To determine the fat of the flour, four grammes are dried and re-

<sup>\*</sup> Bread Analysis, London, 1886, p. 43.

peatedly digested with ether until exhausted. The filtrates are evap orated in a tared vessel and weighed.

To determine the ash, ten grammes of the flour are incinerated in platinum capsule to a white ash, which is then weighed.

Among the adulterations of flour, besides the admixture of othe starchy material of lesser value, which must be looked for with the micro scope (see starches, p. 185), the most frequently occurring is alum. Fo the detection of this, one of the best known tests is based upon the pror erty of alumina of forming a violet- or lavender-colored lake with th coloring matter of logwood. Ten grammes of the flour should be mixe in a wide beaker with ten cubic centimetres of water, one cubic cent metre of the logwood tincture (five grammes of logwood-chips digeste with one hundred cubic centimetres of strong alcohol) and an equa measure of a saturated aqueous solution of ammonium carbonate ar then added, and the whole mixed together thoroughly. If the flour i pure, a pinkish color, gradually fading to a dirty brown, is obtained whereas if alum be present, the pink is changed to a lavender or actual blue. As a precaution, it is desirable to set the mixture aside for a fer hours or to warm the paste in the water-oven for an hour or two and not whether the blue color remains.

To determine whether flour has been bleached with nitrogen peroxid or not, two tests have been employed. The first is to shake up twenty five grammes of the flour in a four-ounce wide-mouthed glass-stoppere bottle with gasoline. After the latter has settled, if the flour had bee unbleached the gasoline will show distinctly yellow; if bleached, it wi remain nearly colorless.

The second test is with the reagents, sulphanilic acid and alpha-napl thylamine chloride solutions, used to detect nitrites in water analysi Ten grammes of the flour, one hundred cubic centimetres of distille nitrite-free water, and four cubic centimetres of each of the reagents as shaken up in a wide-mouthed, glass-stoppered bottle. With bleache flour a pink or red tint will be developed. For the quantitative dete mination of nitrites in flour, this latter test, known as the Griess-Ilosva reaction, is carried out with special precaution, and the results compare with those obtained from a standard sodium nitrite solution. (S. Leach, Food Inspection and Analysis, 2d ed., p. 321).

2. For Bread.—The methods just described under flour are almo all equally applicable to the baked bread. To test bread for adulteration from alum a slightly different procedure is to be followed. To about wineglassful of water in a porcelain capsule five cubic centimetres freshly-prepared tincture of logwood and the same quantity of the carbonate of ammonia solution are added. A piece of the crumb of the bread, say about ten grammes, is then soaked therein for about find minutes, after which the liquid is poured away and the bread is drive at a gentle heat. If alum be present the bread will acquire a lavend color or more or less approaching dark blue, according to the quantity the alum which has been added; whereas if the color be a dirty brow

the bread may be regarded as pure.

#### F. THE MANUFACTURE OF VINEGAR.

Under the general heading of fermentation mention was made of the acetic fermentation, which frequently follows the alcoholic fermentation. It is produced, it is true, by other species of ferments, but largely upon materials susceptible to the alcoholic fermentation or already changed by it into alcohol-containing products. The close association in nature of these two changes is readily understood when the chemical relationship of alcohol and acetic acid is looked at. The latter is the simple oxidation product of the former, and the processes for developing the alcoholic change in any sugary liquid, such as a beer-wort or a grapemust, have to be controlled carefully that they do not allow of this supplementary change whereby the alcohol goes over into acetic acid. The conditions under which the acetic fermentation sets in may be summarized as follows:

- 1. A liquid weak in alcohol, containing not more than twelve per cent. by weight of this compound.
  - 2. Abundant access of air.
  - 3. A temperature of from 20° to 35° C. (68° to 95° F.).
- 4. Acetic ferments (Mycoderma aceti, etc.), together with the food necessary for these organisms. Under this heading of acetic ferments Nägeli distinguishes besides the Mycoderma aceti, the Mycoderma cerevisiae and Mycoderma vini, although the latter of these is said by De Seynes to arrest the growth of the acetic ferment proper. Hansen also mentions a second ferment as found at times in beer along with the Mycoderma, or, as it is often termed now, Bacterium aceti, to which he gives the name Bacterium Pasteurianum.

The acetic ferment, as before stated (see p. 203), develops not by the budding process characteristic of the yeast ferment, but by splitting or fissure of the elongated cell. When these germs, which originally drop from the air, like the yeast-cells, into the fermenting or sugary liquids, find a liquid specially suited for their growth, as, for example, a mixture of wine and vinegar, they develop rapidly over the surface of the liquid, where they have the necessary oxygen supply, and form a gelatinous skin, which thickens and falls to the bottom of the vessel because of its increasing weight. Another skin forms at once again, and this in turn is replaced by a third, and so on until the liquid is completely exhausted of assimilable material. This skin, called the "mother of vinegar," consists of a multitude of these minute fissure ferments.

#### I. Raw Materials.

Only such materials will be considered here as give rise to a vinegar by the normal acetic fermentation. The manufacture of acetic acid and technically important acetates will be spoken of later under pyroligneous acid as derived from the destructive distillation of wood.

The materials referred to as furnishing vinegar under the influence of the acetic fermentation are, first, wine; second, spirits; third, maltwort or beer; fourth, fermented fruit juices other than wine; and, fifth, sugar-beets.

The wines used are both red and white wines, and are such as are of inferior vintages, and considered unfit for drinking as wine. Such wines are gathered together from all sections and are made into vinegar largely in France at Orleans and at Paris. The wines do not exceed ten per cent. alcoholic strength. Wines about a year old are the best for vinegar-making, as the new wines are prone to undergo putrid or ropy fermentation, and older wines do not contain sufficient extractive matter.

The spirits used are chiefly the potato brandy of Germany and whiskey in this country, the vinegar in either case being made by the "quick-vinegar" process. These spirits, when used for vinegar-making, are so diluted with water and vinegar already formed that the alcoholic strength ranges between three and ten per cent.

The malt-wort used for vinegar-making is exactly like that prepared for grain spirit manufacture, unmalted grain and malt being used admixed, and the alcoholic fermentation being pushed so as to produce the maximum amount of alcohol from the converted starch of the grain. When the alcoholic fermentation is completed it is allowed to stand for some days in the fining-vats, where all dead yeast and cloudiness subside, and it is then made to pass through a filter-bed of wood-chips into the acetifier. The unmalted grain used in the preparation of the wort must be thoroughly dried in a kiln previous to crushing in order that many of the glutinous and albuminoid matters may be destroyed. These would otherwise interfere with the keeping qualities of the vinegar. Sour ale or beer is said not to yield good vinegar, but a product very liable to undergo putrid fermentation, a very disagreeable smell being imparted to the vinegar in consequence.

Cider from apples and Perry from pears are about the only fruit juices besides wine fermented for the production of vinegar. Cider from good, sweet, and ripe apples serves for the manufacture of cider vinegar in this country. The cider is the product of a spontaneous alcoholic fermentation of the apple juice, and the vinegar formation may be merely a continuation of this spontaneous change, but much is now made by the quick-vinegar process, using casks containing beechwood shavings.

Sugar-beets are used somewhat in France for vinegar-making. The beets are rasped to a fine pulp and pressed. The juice is diluted with water and boiled. After cooling, yeast is added and the alcoholic fermentation developed, and this product mixed with vinegar and treated as the other alcoholic liquids before mentioned for the development of the acetic fermentation.

Artificial glucose, cane-sugar, and molasses have also been used in England for the production of vinegars which are used to adulterate malt vinegar.

## II. Processes of Manufacture.

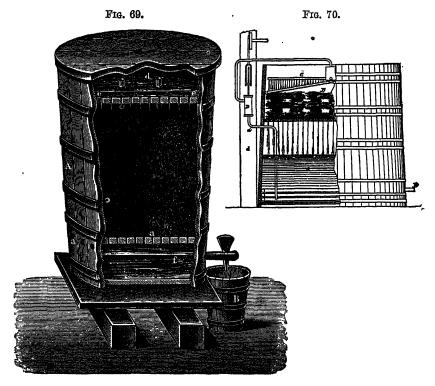
1. The Orleans Process.—This is the process by which wine vinegar is made in France and Germany, and is the oldest in practical use of the several methods now employed. The wine which is to be acetified is allowed to stand for a time over wine-lees, and then clarified by being passed through vats containing beech-shavings. The oaken acetifying

vessels, holding from fifty to one hundred gallons, known as "mothercasks," are first steamed out and then soured with boiling vinegar, which is made to fill one-third of the cask. The wine is now added in instalments of ten litres every eight days until the cask has become more than half-full, when one-third of its contents are siphoned off into storagevats and the periodical addition of wine continued as before. "mother-casks." or acetifiers, can be used in this way continuously for vears until the sediment of yeast, argols, and impurities makes it necessary to give them a thorough cleaning. The vinegar obtained in this way has a very agreeable aroma, that made from white wines being most When the wines employed in the Orleans process are too weak it often happens that the vinegar is ropy and wanting in transparency. In such case it must undergo the firing process. The progress of the acetification is judged of by plunging in a rod and examining the froth upon it when withdrawn. This should be white and copious. The temperature that is found to answer best is between 24° and 26.6° C. (75° and 80° F.)

Hengstenberg has proposed a modification of the Orleans process, whereby a series of the "mother-casks" are connected together at the base by short pieces of glass tubing. After the acetification of the first addition of wine in each cask the new wine is added only to the first cask, into which it runs slowly, while from the last cask of the series, by means of a siphon-tube fixed in the side, the excess flows off as finished vinegar. The increase of yield by this modification is, however, only slight.

2. THE QUICK-VINEGAR PROCESS.—This process was first introduced by Schutzenbach in 1823, and has been considerably improved since. It is used exclusively in the case of spirit vinegar in Germany and in this country, and, with slight modifications, in England for malt vinegar. The vinegar-formers are upright casks from six to twelve feet in height and three to five feet in diameter. About a foot above the true bottom of the cask it has a false bottom perforated like a sieve. Upon this beech-wood shavings are heaped, extending nearly to the top of the cask. Between the true and false bottoms and just under the latter a series of holes is bored in the cask in a direction slanting downward and extending around the entire cask. The beech-shavings are first boiled in water and dried. They are then soured or soaked in warm vinegar for twentyfour hours, filled into place and covered by a wooden disk perforated by fine holes in which pack-thread is loosely filled. This disk also is perforated by four larger glass tubes open at both ends, which serve as air-vents. The cask is then closed on top by a wooden cover with a single hole in the centre, through which the alcoholic liquid is to be poured and from which air may escape. The entire arrangement may be understood from Fig. 69. During the oxidation of the alcoholic liquid considerable heat is developed, and a current of air is thus made to enter through the circle of holes under the false bottom and rise through the wet shavings, escaping through the opening at the top. The diluted spirits or mixture to be acetified are poured into the top of each vat, and as they

flow off, by the aid of a siphon arrangement from the base they are introduced into the top of the second vat. If not over four per cent. of alcohol were contained in the original liquid, that drawn off from the second vat will be converted into good vinegar. The temperature of the vinegar-forming casks should be about 35° C. (95° F.). Above this there is too much loss of alcohol and aldehyde by evaporation; below it, the oxidation goes too slowly. If the minute organisms known as "vinegar eels" show themselves, hot vinegar is poured in on top until it shows a temperature of 50° C. (122° F.) on running off, which kills them.



Whiskey, brandy, and grain spirit properly diluted are all acetified by the aid of this quick-vinegar process. To these diluted spirits a small amount of malt infusion is generally added to furnish nutritive matter for the development of the acetic ferment, which in this process as in the preceding is the agency whereby the atmospheric oxidation becomes effective in changing alcohol into acetic acid.

3. Manufacture of Malt Vinegar.—This is effected by a process much resembling the quick-vinegar process. The acetifiers are, however, much larger, holding from eight thousand to ten thousand gallons. Their construction is shown in Fig. 70. Bundles of birch-twigs, B, are supported upon a perforated bottom, from which the liquid trickles in fine streams. The malt-wort fed in below is warmed by a closed steam-coil of block-tin, and pumped to the top of the casks, where it is sparged, or

sprinkled, in fine streams over the birch-twigs, and the process repeated until the vinegar shows the requisite strength. These birch-twigs have been previously freed from all juice and coloring matter by repeated boiling with water, and are soured before starting the sparging. The entire process of making malt vinegar requires about two months. The temperature at the beginning of the process is about 43° C. (110° F.), and later is kept at 38° C. (100° F.).

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- 4. The Manufacture of Cider Vinegar.—As before stated, this is largely a spontaneous fermentation. The fresh cider is allowed to ferment in barrels having the bung-hole open, which are exposed to the sun or placed in a warm cellar. The acetification is often made a progressive change by adding fresh quantities of cider to the barrel every few weeks; the addition of "mother of vinegar" also is made to accelerate the change.
- 5. Pasteur's Process for Vinegar-making by Direct Use of the Vinegar Fungus.—Pasteur takes an aqueous liquid containing two per cent. of alcohol and one per cent. of vinegar and small amounts of phosphates of potassium, magnesium, and lime, and in this propagates the acetic ferment (Mycoderma aceti). The plant soon spreads out and covers the whole surface of the liquid, at the same time acetifying the alcohol. When one-half of the alcohol has been changed small quantities of wine or alcohol mixed with beer are added daily until the acetification slackens, when the vinegar is drawn off and the "mother of vinegar" collected, washed, and used again with a freshly-prepared mixture. When wine or beer is used, the addition of the phosphate salts as food for the plant is unnecessary, but when pure alcohol is used they are needed. Vinegar prepared by this process is said to possess the agreeable aroma of wine vinegar.

#### III. Products.

Wine Vinegar varies in color from light yellowish to red, according as it has been derived from white or red wines, that from the former being the most highly esteemed. The vinegar from red wines, however, can be decolorized by filtration through purified bone-black. Skimmed milk is also used for the same purpose. When thoroughly agitated with the vinegar the casein coagulates and carries down with it the greater part of the coloring matter of the vinegar, besides clarifying it. It is not used, however, so much as the filtration through charcoal. Wine vinegar has a specific gravity 1.014 to 1.022, and contains from six to nine per cent. (rarely twelve) of absolute acetic acid. When freshly made, it contains traces of alcohol and aldehyde. The amount of acid potassium tartrate (tartar) contained in wine vinegar averages .25 per cent. Its presence is peculiar to this variety of vinegar.

Malt and Beer Vinegars have a higher specific gravity (1.021 to 1.025) and contain dissolved dextrine, maltose, soluble albuminoids, and similar constituents of the malt extract. This kind of vinegar on evaporation leaves a glutinous residue only sparingly soluble in alcohol. It contains from three to six per cent. of acetic acid.

Spirit Vinegar is colorless as produced, but is frequently colored with caramel-color to imitate the appearance of wine or cider vinegar. It contains from three to eight per cent. of acetic acid, although the so-called "vinegar essence" (double vinegar) may contain as much as fourteen per cent.

Cider Vinegar is yellowish-brown, has an odor of apples, a density of 1.013 to 1.015, and contains from three and a half to six per cent. of acetic acid. It is distinguished from the other varieties by yielding on evaporation a mucilaginous extract smelling and tasting of baked apples and containing malic acid, which replaces the tartaric acid of the wine vinegar. The differences between cider vinegar and whiskey vinegar as manufactured in this country are shown in the accompanying analyses by Battershall:\*

	Cider vinegar.	Whiskey vinegar.
Specific gravity	1.0168	1.0107
Specific gravity of the distillate from		
neutralized sample	0.9985	0.9973
Acetic acid	4.66	7.36
Total solids	2.70	0.15
Total ash	0.20	0.038
Potassa and phosphoric acid in ash	Considerable.	None.
Heated with Fehling's solution	Copious reduction.	No reduction.
Treated with basic lead acetateF	locculent precipitate.	No precipitate.

Glucose, or Sugar, Vinegar, prepared from different saccharine and amylaceous materials by conversion with dilute acid, followed by fermentation and acetification, contains dextrose, dextrine, and often calcium sulphate (from commercial glucose). It is said to be employed in France and England for adulterating wine or malt vinegars.

Factitious Vinegars are often made from pyroligneous acid flavored with acetic ether and colored with caramel-color. Such a product differs from malt vinegar in containing no phosphates, and from wine or cider vinegar in the absence of tartaric or malic acids respectively.

## IV. Analytical Tests and Methods.

The determination of the acetic acid is usually done by titration with standard alkali, using phenolphthaleïn as indicator. In the presence of free sulphuric acid, it is necessary to distil a measured quantity of the sample almost to dryness and titrate the distillate, it being assumed that eighty per cent. of the total acetic acid present passes over.

The determination of the extract or solid residue in vinegar is executed in the same manner as described under beer or wine.

The test for *sulphuric acid* is an important one. In England, the manufacturers were allowed by law to add one part of sulphuric acid by volume to one thousand of vinegar in order to protect weak vinegar from the putrid fermentation. This addition is not necessary in good vinegar and is not generally followed at present. Still, it may be present, and is to be looked for in all vinegars. The usual test with basic chloride is

<sup>\*</sup> Food Adulteration and Detection, New York, 1887, p. 230.

inoperative here, as sulphates may be present in the vinegar from the water used, etc. Hehner's test for free mineral acids (sulphuric and hydrochloric), now regarded as satisfactory in this case, is based on the fact that acetates and most other salts of organic acids are decomposed by ignition into carbonates, having an alkaline reaction to litmus, while sulphates and chlorides of the light metals are unchanged on ignition and possess a neutral reaction. To determine the amount of free mineral acid it is sufficient therefore to carefully neutralize the vinegar with standard solution of soda before evaporation to dryness (the same process serving for a determination of the total free acid), ignite the residue, and titrate the aqueous solution of the ash with standard acid. If the free acid originally present were wholly organic, the ash will contain an equivalent amount of alkaline carbonate, which will require an amount of standard acid for its neutralization exactly equivalent to the amount of standard alkali originally added to the vinegar. Any deficiency in the amount of standard acid required for neutralization is due to the free mineral acid originally present in the vinegar.

The tartaric acid, a normal constituent of wine vinegar, may be tested for by evaporating to dryness and treating the extract with alcohol, which dissolves nearly everything but the tartar or acid potassium tartrate. On pouring off the alcohol and dissolving this in a little hot water its nature can be easily shown by the usual tests for tartaric acid.

Caramel is recognized by extracting the solid residue with alcohol and evaporating the solution to dryness; in its presence the residue now obtained will possess a decidedly dark color and a bitter taste.

Metallic impurities, such as lead, copper, and zinc, are at times to be found arising from the use of metallic vessels for storing the vinegar. Arsenic has also been found as an impurity through the use of impure sulphuric or hydrochloric acid. They are all detected by the usual qualitative tests.

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#### STATISTICS.

#### I. PRODUCTION OF HOPS THROUGHOUT THE WORLD. .

From the U. S. Consular Reports the total crop of hops throughou the world for the last three years is given as follows:

#### TOTAL CROP IN CWT. OF 110 LBS.

Countries	1909	1910	1911
Germany	119,000	384,000	222,000
Austria-Hungary	164,000	297,000	178,000
France	27,000	54,000	45,000
Belgium and Holland	29,000	58,000	52,000
Russia	60,000	58,000	62,000
England	205,000	296,000	354,000
America	310,000	400,000	400,000
Australia	10,000	10,000	15,000
•			
	924,000	1,557,000	1,328,000

The United States imports a limited quantity of hops, but exports much larger amount. The figures for recent years were:

	1906.	1907.	1908.	1909.	1910.
Imports in pounds	9,630,206	5,733,386	8,636,192	7,383,907	3,185,99
Valued at	\$2,266,333	\$1,813,306	\$1,911,602	\$1,335,300	\$1,492,77
Exports in pounds					
Valued at					

## II. a. BEER PRODUCTION IN THE UNITED STATES.

According to the reports of the Commissioner of Internal Revenue, there were brewed in the United States the following amounts of malt liquors:

	•	Bbls. (31 gallons
		Bbls. (31 gallons or 117.3 litres).
1905	 	. 49,459,540
1906	 	. 54,724,553
1907	 	. 58,546,111
1908	 	. 58,747,680
1909	 <i>.</i>	. 56,364,360
1910	 	. 59,544,775

## II. b. PRODUCTION OF DISTILLED SPIRITS IN THE UNITED STATES (IN GALLONS).

	From grain and cereals.	From fruit.	Totals.
1906	145,666,125	4,444,072	150,110,197
	168,573,913	6,138,305	174,712,218
1908	126,989,740	6,899,823	133,889,563
1909	133,450,755	6,440,859	139,891,613
	156,237,526	7,656,433	163,893,960

#### II. C. BEER PRODUCTION AND CONSUMPTION OF THE WORLD FOR 1904 AND 1905.

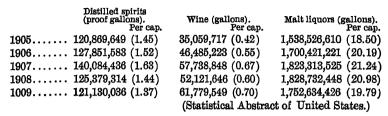
	Production	in hectolitres.	Consum capita i	ption per n litres.
	1904.	1905.	1904.	1905.
Great Britain	56,395,360	54,842,670	129.60	124.65
Russia	6,560,140		4.54	
Norway	295,020	307,890	13.05	13.50
Sweden	2,751,210		52.20	
Denmark	2,451,460	2,415,010	92.25	92.25
Germany	69,538,590	72,027,450	115.65	118.35
Belgium	15,163,830	15,592,500	216.90	219.60
France	14,125,320	13,283,820	34.45	33.75
Switzerland	2,093,850		64.35	
Italy	227,700	235,620	0.90	0.99
Austria	19,621,800	10,908,010	68.40	64.35
Hungary	1,500,840	1,485,990	8.10	8.10
Bulgaria	64,340	88,110	1.67	2.21
Servia	75,240		2.97	
United States	57,546,310	63,591,840	68.80	75.60
9	248,410,000	245,778,910	58.25	68.48

(English Parliamentary Report on Alcoholic Beverages, 1905.)

## III. WINE PRODUCTION OF THE WORLD FOR 1897 AND 1898.

	1897.	1898.
	Hectolitres.	Hectolitres.
France	32,350,700	32,282,300
Algeria and Tunis	4,457,758	5,341,000
Italy	25,958,500	31,500,000
Spain	18,900,000	24,750,000
Portugal	2,500,000	2,100,000
Austria-Hungary	3,000,000	2,800,000
Russia	2,500,000	3,120,000
Switzerland	1,250,000	1,160,000
Germany	2,775,576	1,406,818
Roumania	3,200,000	3,900,000
United States	1,147,000	1,300,000
Other countries	10,261,000	9,975,000
:	108 300 534	119.635.818

IV. G. CONSUMPTION OF SPIRITS, WINES, AND MALT LIQUORS IN THE UNITED STATES



IV. b. CONSUMPTION OF SPIRITS, WINES, AND BEER DURING 1901-1908 PER CAPITA I DIFFERENT COUNTRIES (IN IMPERIAL GALLONS).

	Spirits.	Wine.	Beer.
Australia	0.89	1.29	11.88
Belgium	1.06	1.02	47.75
Canada	0.86	0.09	5.01
Denmark	2.54		20.58
France	1.35	30.67	7.92
Germany	1.55	1.45	26.25
Holland	1.50	0.37	6.50
Italy	0.25	25.04	0.14
Norway	0.62		3.45
Russia	0.94		0.98
Sweden	1.46		12.60
Switzerland	0.97	13.65	13.88
United Kingdom	1.00	0.32	29.45
United States	1.45	0.52	18.50
(Webb,	Dictionary	of Statistics,	1910.)

#### CHAPTER VII.

#### MILK INDUSTRIES.

#### I. Raw Materials.

Milk is the fluid secreted by the females of the mammalia for the nourishment of their young, and is therefore a food specially adapted for the needs of the animal organism at this stage, furnishing all the nutrients required and furnishing them in the proper proportion. As will be seen from its analysis, it occupies an intermediate position between the cereal and the strictly animal foods, approximating, of course, more nearly the latter, but showing in one important constituent, milk-sugar, its relationship to the former.

Milk is a secretion of the mammary glands, in which it is produced proximately by certain processes of diffusion from the blood and immediately by the breaking down of the gland-cells themselves, so that milk is described as cell-material liquefied. The milk of all mammalia is essentially the same in its constituents, although these vary somewhat in their relative proportions.

The essential constituents of milk are water, fat, casein, albumen, milk-sugar, and salts. The relative proportion of these constituents in the milk of different animals may be seen from the following table of analyses from Wynter Blyth:\*

	Fat.	Casein.	Albu- men.	Milk- sugar.	Ash.	Total solids.	Water.
Human milk Cow's milk	2.90	2.40	0.57	5.87	0.16	12.00	88.00
	3.50	3.98	0.77	4.00	0.17	13.13	86.87
Camel's milk	2.90	3.	84	5.66	0.66	18.06	86.94
Goat's milk	4.20	8.00	0.62	4.00	0.56	12.46	87.54
	1 02	1.09	0.70	5.50	0.42	8.83	91.17
	2.50	2.19	0.42	5.50	0.50	11.20	88.80
	5.30	6.10	1.00	4.20	1.00	17.78	82.27

In taking up milk as a raw material for industrial utilization, we shall refer to cow's milk exclusively unless otherwise specified.

The fat exists in the milk in the form of minute globules suspended in a thin liquid, forming for the time a perfect emulsion with the aqueous solution of the other constituents. The fat is essentially an intimate

<sup>\*</sup> Foods, Composition and Analysis, 1882, pp. 214, etc.

mixture of the glycerides of the fatty acids, palmitic, stearic, and ole not soluble in water, and of the glycerides of certain soluble volati acids, such as butyric, caproic, caprylic, and capric.

The casein of milk exists in the fresh milk as a diffused colloid compound of albumen and calcium phosphate, which by the action rennet (a ferment from the calf's stomach) is converted into the i soluble one known as casein. The casein precipitated by rennet co tains five to eight per cent. of ash, consisting almost entirely of calciu phosphate. If, however, this calcium phosphate compound of album is decomposed by mineral acids or acetic acid, the casein precipitate contains only traces of ash. Lactic acid gives the same result, so th the casein coagulated by the souring of the milk shows less ash the that precipitated by rennet from sweet milk. On the other hand, carbo dioxide will act like rennet. The soluble compound existing in the free milk is considered to be that of the tricalcium phosphate with albume while the insoluble one precipitated by rennet is the acid calcium pho phate with albumen. Pure casein is a perfectly white brittle crumbling substance, insoluble in water, but soluble in very dilute acids or ver dilute alkalies. In the action of rennet and acids upon casein a portic is apparently altered into what are called peptones (lacto-protein lacto-peptone) and remains dissolved in the whey of the milk. The albumen (or soluble nitrogenous matter) of milk seems to be analogous to the albumen of blood. It may be obtained by precipitation with bas acetate of lead or by dialysis as a yellowish flaky mass. The proportion of albumen in milk is always, according to Wynter Blyth, about on fifth of the casein.

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Two additional nitrogenous compounds have been found by Blyth exist in small amounts in milk, to which the names galactine and lact chrome have been given.

Milk-sugar, which is an important and characteristic constituent the milk, is obtained from the serum, or "whey." After the separatic of the curd has been effected by the addition of rennet the whey evaporated on the water-bath, and yields the milk-sugar in hard cry tals. These when purified by animal charcoal and recrystallized sho the composition  $C_{12}H_{22}O_{11}+H_2O$ . It is easily distinguished from the sugars of the same formula. It is converted by boiling with dilute acids into dextrose and galactose, which latter has one-fifth le copper-reducing power than dextrose. It undergoes the lactic fermentation readily but the alcoholic with some difficulty.

The ash of milk consists of calcium citrate and the phosphates an chlorides of potassium, sodium, calcium, and magnesium, the salts the are specially needed for the growth of the bone-material in the your nourished by the milk.

Cow's milk is a white or yellowish-white liquid nearly opaque, except in very thin layers, when it has a bluish opalescent appearance, an a specific gravity of from 1.029 to 1.035. It has a mild sweetish tas and a slight but characteristic odor, stronger when still warm from the

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cow. Upon allowing milk to remain at rest for some time it undergoes two changes: First, a yellowish-white layer forms on the surface known as "cream," due to the rising of the specifically lighter fat-globules from the body of the liquid where they were held back in emulsion with the aqueous liquid; and, second, the aqueous liquid after a time undergoes further separation into a thick coagulum or "curd" of casein and a thinner liquid or "whey," holding the sugar of milk, any lactic acid formed from it, and the salts in solution. Both of the changes are of the greatest importance, as upon them are based the great milk industries, butter-making and cheese-making respectively.

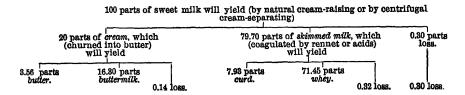
The rising of the cream is largely dependent ordinarily upon two conditions: First, the temperature,—a low temperature being favorable to the separation; and, second, complete freedom from agitation. These conditions are not, however, indispensable, as will be seen later. (p. 282) in speaking of the use of centrifugals for the separation of cream.

The rising of the cream is generally allowed to be an entirely spontaneous change on the part of the milk and the first one which it undergoes, but in some creameries a little sour milk (containing lactic acid) is added to the fresh milk, when first put in the cream-rising pans, so that the curdling of the casein may facilitate the escape of the fatglobules and the rising of the cream. In such a case what remains on removal of the cream is not ordinary skimmed milk, but a sour curdled milk. The second change mentioned, that of curdling, is really preceded by a change of some of the milk-sugar into lactic acid (due to lactic fermentation, which sets in very quickly in hot weather or if the milk has not been kept in clean vessels). This souring of the milk may be retarded by the addition of a little carbonate of soda or boric acid. The lactic acid as soon as liberated decomposes the soluble casein compound, before referred to (see p. 279), and the case in is thrown out or coagulated as "curd." The separation of the curd is aided by heat. The liquor in which this coagulated casein floats, the serum of milk, or "whey," contains about one-fourth of the nitrogenous matter of the milk, all of its sugar, and most of its mineral matter. The whey is "sour whey" in case lactic acid has formed as the antecedent of the coagulation, or "sweet whey " in case the casein is thrown out by the action of rennet without the formation of lactic acid.

The composition of the several parts into which the milk is divided by these changes is thus given by Fleischmann:

	Water.	Fat.	Casein.	Albumen.	Milk-sugar.	Ash.
Whole milk	87.60	8.98	8.02	0.40	4.30	0.70
	77.30	15.45	8.20	0.20	3.15	0.70
	90.84	1.00	2.87	0.45	4.63	0.71
	14.89	82.02	1.97	0.28	0.28	0.56
	91.00	0.80	8.50	0.20	8.80	0.70
	59.80	6.43	24.22	3.53	5.01	1.51
	94.00	0.35	0.40	0.40	4.55	0.60

And the relative yield of these several constituents from one hundred parts of milk is thus given by the same author:



#### II. Processes of Manufacture.

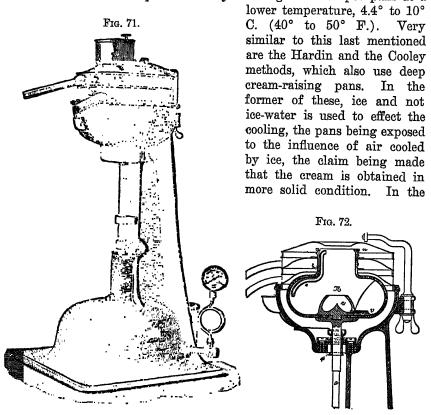
1. Manufacture of Condensed and Preserved Milk.—Condensed milk is milk from which a large portion of the water originally present has been driven off, increasing, of course, in a proportionate degree the percentage of the other constituents. This condensed product may or may not have cane-sugar added to it as a preservative. That to be preserved with cane-sugar is made much more concentrated, and is that which is manufactured for export and preservation in sealed tin cans. In its preparation, the milk is first heated to 65.6° to 80° C. (150° to 175° F.) by placing the cans containing the milk in hot water, and is then strained and conveyed to the evaporating vessels, which are usually vacuum-pans. Refined sugar is added during the boiling to the amount of one to one and a half pounds for every quart of the condensed milk produced. The product is drawn off into cans, cooled to about 70° F., and then weighed into tins, which are at once soldered down.

Condensed milk free from cane-sugar is only concentrated to about one-half the degree attained in the other product, and is then cooled and filled into stone or glass flasks provided with ordinary air-tight stoppers. It will remain fresh for from one to two weeks, and requires only to be diluted with its own bulk of water in order to yield the counterpart of the original milk.

Preserved milk is either prepared by Appert's process, which consists in boiling the milk to destroy ferments and keeping it then in hermetically-sealed vessels, or by Scherff's improved process, whereby the milk is filled into glass bottles which are stopped with corks previously steamed and then fastened in by clamps, and then heated in closed boilers under a pressure of from two to four atmospheres to about 120° C. The bottles are then taken out of the pressure-vessel and cooled down, with the corks covered with flannel soaked in paraffin, so that as they cool the air entering through the pores of the corks shall be filtered. When cooled down, the cork, which has been drawn into the neck of the bottle considerably, is covered with a layer of paraffin. This kind of preserved milk is used largely in Germany for invalids and children.

2. OF BUTTER.—The first operation in this connection is the separation as completely as possible of the cream from the rest of the milk. This is generally a spontaneous process, it is true, but its completeness is dependent largely upon the conditions before referred to. There are

various ways in which the raising of the cream is allowed to take place. We may mention the Holstein process, in which the fresh milk is at once set to raise cream in wide shallow pans at a temperature of 12° to 15° C. (53.6° to 59° F.), the Dutch process, in which it is first rapidly cooled down in large vessels immersed in cold water to about 15° C. (59° F.) and then transferred to the shallow pans for the raising of the cream, and the Schwartz process, largely used in Northern Europe, which differs from the Dutch process chiefly in using much deeper pans at a



Cooley method, used largely in this country, the water not only surrounds the can outside as high as the milk inside, but is made to rise an inch or two above the lid, so that the can is completely submerged and all contamination from external sources prevented.

The processes which use shallow pans give a larger yield of cream but take a longer time (thirty-six to forty-eight hours as against eighteen to twenty-four for those using deep pans). Within twenty years past the principle of the centrifugal has been applied to the separation of the cream from the milk, and this has proven itself so successful that in most large creameries it is now utilized. The milk is placed in a horizontal rotating vessel driven at a high rate of speed, which causes the heavier milk fluid to gravitate towards the circumference of the vessel,

whilst the cream remains nearer the centre and rises towards the upper part of the rotating bowl, whence it is removed by a conveniently-place aperture on the side of the vessel. An exit is also provided for the gradual removal of the skimmed milk, thus making room for fresh mit to be added to the apparatus and allowing the process to be carried a continuously. Figs. 71 and 72 show the Laval cream separator in general view and in section. The fresh milk is admitted through a funne the tube of which is prolonged so as to deliver the milk near the botto of the revolving drum. The skim-milk flows out through an opening, and the cream through a higher opening, the relative position of whice can be changed by an adjustable screw above. The cream obtained a these centrifugal separators seems to be freer from mechanical enclosed casein than that gotten in any of the old separation processes is seen in the appended cream analyses by Bell,\* where samples 2 ar 6 were separated by the centrifugal separator:

												Water.	Fat.	Milk- sugar.	Casein.	Ash.
1. 2. 3. 4. 5. 6.	Raw cream Raw cream Raw cream Raw cream Raw cream Thick cream Devonshire c	tto	·	cr	ca		 	 	 	:	 	54.02 60.66 67.98 58.07 63.07 87.62 83.76	39.40 33.60 24.44 35.67 30.74 58.77 59.79	1.85 2.43 2.96 2.20 2.61 1.46 1.01	3.76 2.90 4.04 3.55 3.04 1.83 4.97	0.57 0.41 0.65 0.51 0.54 0.82 0.47

The composition of the skimmed milk of course varies according the extent to which the cream has been removed. The following analys by Voelcker represent its average composition as obtained in the ordinal way and as obtained by the Laval separator:

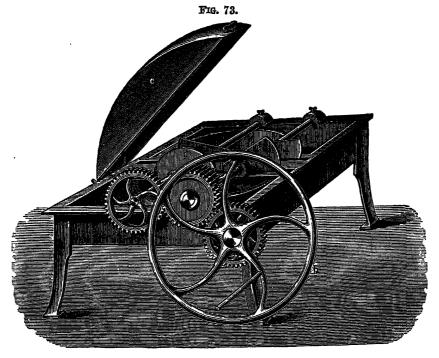
•	Water.	Butter- fat.	Casein,	Milk- sugar.	Ash.
Ordinary skimmed milk	89.25	1.12	3.69	5.17	0.78
	90.82	0.31	3.81	4.77	0.79

The coalescence of the fat-globules separated in the cream layer now to be effected to form the compact butter. This is almost unive sally accomplished by mechanical agitation in the process called churing. The churns may be of very diverse construction, either for han or power. The cream may be taken as "sweet cream" freshly separate in the centrifugal or raised from deep pans where the skim-milk is sti sweet, or it may be "sour cream," which has stood longer and he separated slowly in shallow pans. The sour cream is more easily churne but the butter will contain more casein, while sweet cream yields a butte with pleasanter taste and better keeping qualities because containing less than the containing the same of the containing the containing

<sup>\*</sup> Analysis and Adulteration of Food, p. 35.

casein. The temperature most favorable for churning is about 15.5° C. (60° F.). Sometimes cream is heated to a much higher temperature first, and then cooled down to 60° F. before being churned. Butter thus made keeps well.

Butter has almost invariably some salt added to it even when for immediate consumption; the quantity in this case need not be large (five-tenths to two per cent.), but when it is to be packed for preservation or for export considerably more is added, so that it is known as "salt butter." Export butter has also a small addition of sugar, and sometimes saltpetre, added, as well as salt, to preserve it. Genuine

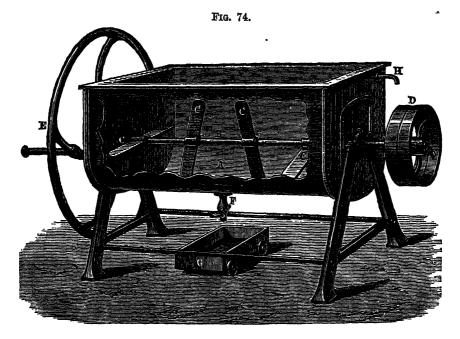


butter will always have a yellowish color, which, however, becomes deeper in summer when the cows have an abundance of fresh pasture. Most butter manufacturers now add a little vegetable coloring matter like annotto, carrot-color, or saffron, to give the butter this desired yellow tint in winter, when the butter would otherwise be very much lighter in color. All butter will in time become rancid and take a strong disagreeable odor. This is due to the gradual spontaneous decomposition of the butyric other under the influence of air and light whereby free butyric acid is liberated.

The composition of butter will be more fully spoken of later on in discussing the products of these industries.

3. OF ARTIFICIAL BUTTER (Butterine, Oleomargarine).—The manufacture of substitutes for normal dairy butter began with the experiments of the Frenchman Mège-Mouries in 1870. He found that carefully-

washed beef-suet furnished a basis for the manufacture of an excellent substitute for natural butter. The thoroughly-washed and finely-chopped suet was rendered in a steam-heated tank, taking for one thousand parts of fat, three hundred parts of water, one part of carbonate of potash, and two stomachs of pigs or sheep. The temperature of the mixture was raised to 45° C. After two hours, under the influence of the pepsin in the stomachs, the membranes are dissolved and the fat melted and risen to the top of the mixture. After adding a little salt, the melted fat is drawn off, stood to cool so as to allow the stearin and palmitin to crystallize out, and then pressed in bags in a hydraulic press. Forty to fifty per cent. of solid stearin remains, while fifty to sixty per cent. of fluid



oleopalmitin (so-called "oleomargarine") is pressed out. Mège then mixed the "oleo oil" with ten per cent. of its weight of milk and a little butter-color and churned it. The fat-cutting process of Mège-Mouries is shown in Fig. 73 and the churning of the "oleo oil" in Fig. 74. The product was then worked, salted, and constituted the "oleomargarine," or butter substitute. Various improvements have been made in the process of Mège, and it has been found that leaf-lard can be worked in the same way as beef-suet, and will yield an oleopalmitin suitable for churning up into a butter substitute.

The processes now followed are given substantially as described by Mr. Phil. D. Armour in his testimony before a committee of Congress:\*
"The fat is taken from the cattle in the process of slaughtering, and after thorough washing is placed in clean water and surrounded with

<sup>\*</sup> Department of Agriculture, Bulletin No. 13, Part i. p. 16.

ice, where it is allowed to remain until all animal heat has been removed. It is then cut into small pieces by machinery and cooked at a temperaaure of about 150° F. (65.6° C.) until the fat in liquid form has separated from the fibrin or tissue, then settled until it is perfectly clear. Then it is drawn into graining-vats and allowed to stand for a day, when it is ready for the presses. The pressing extracts the stearin, leaving a product commercially known as 'oleo oil,' which when churned with cream or milk, or both, and with usually a proportion of creamery butter, the whole being properly salted, gives the new food product, oleomargarine. In making butterine we use 'neutral lard,' which is made from selected leaf-lard in a very similar manner to oleo oil, excepting that This neutral lard is cured in salt brine for no stearin is extracted. forty-eight to seventy hours at an ice-water temperature. taken and with the desired proportion of oleo oil and fine butter is churned with cream and milk, producing an article which when properly salted and packed is ready for the market.

"In both cases coloring matter is used, which is the same as that used by dairymen to color their butter. At certain seasons of the year—viz., in cold weather—a small quantity of sesame oil or salad oil made from cotton-seed oil is used to soften the texture of the product."

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It will be seen that in this process a higher temperature is used in rendering the fat than was used originally by Mège. He obtained about fifty per cent. of oleo oil. The manufacturers now obtain sixty-two per cent. or more. The oleo oil from beef-suet and the neutral lard from leaf-lard are frequently mixed, the proportions varying according to the destination of the product; a warm climate calling for more "oleo," a cold one for more "neutral." In ordinary practice about forty-eight gallons of milk are used for churning with the oil per two thousand pounds of product. Plain oleomargarine is the cheapest product made. By adding to the material in the agitator or churn more or less pure butter what is known as butterine is produced, two grades of which are commonly sold,—viz., "creamery butterine," containing more, and "dairy butterine," containing less, butter.

Large quantities of oleo oil are now manufactured and exported as such from the United States to Europe, notably to Holland, where it is made up into oleomargarine butter. There are said to be seventy manufactories of this kind in Holland which work up oleo oil from all parts of the world.

4. Cheese-making.—The manufacture of cheese depends upon the property possessed by casein of being curdled by acids or ferments. In the case of sour milk, the milk-sugar has developed by the lactic fermentation some lactic acid, and this, as before stated, promptly throws out the casein in the insoluble form. In the case of sweet milk we usually accomplish the curdling of the casein not by the use of an acid, but with a ferment contained in the preparation called rennet. This is prepared from the fourth stomach of the calf by first cleansing the stomach, cutting and drying it, and then leaving some brine in contact with its lining membrane for a few days. The salt liquid will thus acquire very

active properties, so that a small quantity will curdle a large quantit of milk. We would have then, according as one or the other method followed, a sour-milk cheese or a sweet-milk cheese. The former have very minor value commercially, being made mainly for immedia domestic consumption. The latter class include all the more valuab commercial varieties. Of these we may distinguish fat, half-fat (medium), and lean cheeses, or as they are also designated to indica their origin, cream cheeses, whole milk cheeses, and skim-milk cheese As these last names indicate, the material may differ. We may have moreover, all gradations or mixtures of cream, whole milk, and skin milk used for the various grades manufactured.

In cheese-making from sweet milk, the milk, whether whole, mixe with cream, or skimmed, is heated to about 30° C. (86° F.) and the rennet added. It curdles usually in from thirty to forty minutes. Aft the curd has formed and been cut, or "broken down," the heat is raise to 98° F. (36° C.) to insure the souring of the whey and its more consplete separation from the curd. Or the curd produced at not over 86° (30° C.) is after being cut collected in a heap, covered with a cloth preserve the heat, and allowed to stand an hour to develop the acidic which serves to harden the curd and promote its separation from the whey. The curd is now cut up, worked to free it from the whey, salted and pressed. After it has acquired sufficient coherence (which requires from twelve to fourteen hours) it is taken from the press and place in the curing-room to "ripen." This ripening process is essentially fermentative one, and during its progress the curd loses its insipidicand acquires the characteristic taste and flavor of cheese.

In this process of ripening, the milk-sugar remaining in the chee becomes transformed partly into lactic acid and partly into alcohol ar carbon dioxide. In some varieties the carbon dioxide swells up ("huffs" the cheese-mass and gives it the porous character so noticeable in tripened cheese.

Fresh cheese has an acid reaction, but this diminshes more and mo in the ripening, as the casein is gradually altered, soluble albuminoic peptone-like bodies, and organic bases like leucine, tyrosine, and amin being formed.

Some cheeses, especially the cream cheeses, are not pressed, but cor on the market as soft cheeses. In these the curdling by rennet has al been effected at a lower temperature than in the case of the hard cheese

Cheese has also been manufactured extensively in this country fro skimmed milk to which oleomargarine or "oleo oil" has been added so to give the finished product the character of a whole-milk cheese. The product is now quite supplanted, however, by the "lard cheese," which according to Caldwell,\* was made in 1882 at over twenty factories the State of New York. In this process an emulsion of lard is made I bringing together in a "disintegrator" lard and skimmed milk be previously heated to 140° F. in steam-jacketed tanks; the "disintegrator

<sup>\*</sup> Second Annual Report New York State Board of Health, p. 529.

consists of a cylinder revolving within a cylindrical shell: the surface of the cylinder is covered with fine serrated projections, each one of which is a tooth with a sharp point; as this cylinder revolves rapidly within its shell the mixture of melted lard and hot skimmed milk is forced up into the narrow interspace; and the lard becomes very finely divided and most intimately mixed, or "emulsionized," with the milk. This emulsion consists of from two to three parts of milk to one of lard. In making the cheese, a quantity of this emulsion, containing about eighty pounds of lard, is added to six thousand pounds of skimmed milk and about six hundred pounds of butter-milk in the cheese-vat, and the lard that does not remain incorporated with the milk or curd, usually about ten pounds, is carefully skimmed off. These quantities of the materials yield from five hundred to six hundred pounds of cheese containing about seventy pounds of lard, or about fourteen per cent. About one-half of the fat removed as cream in the skimming of the milk is thus replaced by lard. It is claimed that no alkali or antiseptic is used, and that only the best kettle-rendered lard can be employed, because of the injurious effect of any inferior article on the quality of the cheese, and that before even this lard is used it is deodorized by blowing steam under eighty pounds pressure through it for an hour. According to many witnesses the imitation is excellent, for experts have been unable to pick out lard cheeses from a lot of these and full-cream cheeses of good quality together.

#### III. Products.

1. Condensed and Preserved Milk.—The distinction between condensed milk prepared with the addition of cane-sugar and that prepared without sugar has already been referred to in speaking of the manufacture of this class of products. The first of these classes forms a white or yellowish-white product of about the consistency of honey and ranging in specific gravity from 1.25 to 1.41. It should be completely soluble in from four to five times its bulk of water without separation of any flocculent residue, and then possess the taste of perfectly fresh sweetened milk.

The second class of condensed milk preparations, those without addition of cane-sugar, are not boiled down to the same degree and remain perfectly liquid, and are put up therefore in glass bottles instead of being sealed in cans. Analyses of both classes are given on the authority of Battershall.\*

Condensed Mil.	k with	Addition	of	Sugar.
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Brand.	Water.	Fat.	Cane- and milk-sugar.	Casein.	Salts.
Alderney Anglo-Swiss (American) Anglo-Swiss (English) Anglo-Swiss (Swiss) Eagle Crown	30.05	10.08	46.01	12.04	1.82
	29.46	8.11	50.41	10.22	1.80
	27.80	8.24	51.07	10.80	2.09
	25.51	8.51	58.27	10.71	2.00
	27.80	6.60	44.47	10.77	1.86
	29.44	9.27	49.26	10.11	1.92

<sup>\*</sup> Food Adult . ti

Condensed Milk without Cane-sugar.

Brand.	Water.	Fat.	Milk-sugar.	Casein.	Salts.
American	52.07	15.06	16.97	14.26	2.80
	56.71	14.13	18.98	18.18	2.00
	55.43	13.16	14.84	14.04	2.53
	56.01	14.02	14.06	18.90	2.01

2. BUTTER AND BUTTER SUBSTITUTES.—Commercial butter is more or less granular, and the more perfect the granular condition the higher is its quality considered. Special effort has been made in the case of oleomargarine or butterine to imitate this granulation, as the artificial product does not naturally tend to show such appearance. A good butter when fresh has a pleasant fragrant odor and agreeable taste, but the flavor, like the color, varies with the food of the cow, certain plants, like garlic, giving a quite pronounced flavor to both milk and butter. At ordinary temperatures butter is easily cut or moulded, and it readily melts to a transparent, light-colored oil. It always contains, according to the thoroughness with which it has been kneaded and washed, more or less easein, which is very liable to undergo decomposition, and hence the necessity for the addition of larger or smaller amounts of salt, which acts as a preservative. When the butter-fat is freed from curd and water by melting the butter and drawing off the oily layer it may be kept for a long time without change.

This butter-fat is made up, as was stated in speaking of the fat of milk, of the glycerides of oleic, palmitic, and stearic acids (the so-called insoluble acids) and the glycerides of butyric, caproic, caprylic, and capric acids (the so-called soluble acids). The proportion in which they exist in butter-fat varies within very slight limits only, so that five to six per cent. may be called the average percentage of the soluble acids, and eighty-eight per cent. the average percentage of the insoluble acids present in butter-fat. This gives a very important means of distinguishing between a natural butter and oleomargarine or natural butter adulterated with the imitations. In such butter the glycerides of the soluble acids (butyric, etc.), are either wanting entirely or, if a little cream was used in the churning with "oleo oil," present in very much smaller amount than the normal. This distinction will be evident from the analyses of normal butter and oleomargine butters, given on the authority of Dr. Bell. \*

Genuine Butter, showing Range of Variation in Composition of the Fat.

	Water.	Salt.	Curd.	Butter- fat.	Specific gravity at 100° F.	Percentage of fixed acids in fat.	Percentage of soluble acids as butyric.	Melting point, Fahren- heit.
1	7.55	1.08	1.15	90.27	913.89	85.56	7.41	85° F.
2	11.71	8.60	0.95	83.74	911.45	88.24	5.41	90° F.
8	11.42	1.29	1.12	86.17	910.47	88.53	4.84	90° F.
4	12.55	0.89	0.74	85.82	910.20	89.00	4.57	90° F.
5	14.62	1.48	1.88	82.02	910.70	89.00	4.50	91° F.

<sup>\*</sup> Analysis and Adulteration of Foods, pp. 68 and 70.

Wa	ter.	Salt.	Curd.	Fat.	Specific gravity at 100° F.	Percentage of fixed acids.	Percentage of soluble acids.	Melting point, Fa. renheit
14. 11. 12. 5. 13.	21 33 32	3.81 1.70 4 00 1.09 8.99	0.48 1.78 1.09 0.67 1.07	81.41 85.86 82.58 92 92 81.78	903.84 902.34 903.15 903.79 901.36	94.34 94.88 95.04 96.29 95.60	0.66 0.47 0.23 0.16	82° F. 78° F. 79° F. 81° F. 78° F.

Analyses of Oleomargarine Butter or Butterine.

The best grades of artificial butter do not differ in appearance from ordinary butter. To induce the proper granulation of the eleomargarin it is chilled thoroughly with fragments of ice immediately after it taken from the churn and before kneading or salting it. In color, consistence, and taste it may be made to imitate the natural butter so as a deceive most persons. A distinction, it is said, however, can always a noted in the taste when it is melted upon hot boiled potatoes, to which imparts a peculiar taste recognizable as distinct from that of a trubutter.

3. CHEESE.—The general classification of the cheeses has been give in speaking of the methods of manufacture, and the distinctions betwee the fat and lean cheeses, between cream cheese, whole-milk and skimmed milk cheeses given. The terms hard and soft cheeses are applied according as the curd has or has not been pressed in the process of manufacturing. Most of the names which have been attached to the different varieties of cheese are those of localities. We will indicate the character of a few of these.

Neufchâtel cheese is a Swiss cream cheese.

Limburger cheese is a soft fat cheese.

Fromage de Brie is a soft French cheese rapidly ripening and devel oping ammoniacal compounds.

Camembert cheese is also a cream cheese.

Roquefort cheese is a cheese made from the milk of the ewe.

Gruyère cheese is a peculiarly flavored Swiss cheese.

Cheddar cheese is a hard cheese made with whole milk.

Single and double Gloucester are made, the first from a mixture of skimmed and entire milk, and the second from the entire milk.

Parmesan cheese is a very dry cheese, with a large amount of caseir and only a moderate percentage of fat.

Eidam cheese is a Dutch cheese, also relatively dry, and covered with red coloring.

In illustration of the chemical composition of these different varieties of cheese we will append three tables, the first of analyses from miscellaneous sources, and the second and third from Bell,\* giving a fuller study of the composition of the cheeses and showing the difference between the fat normally belonging to the cheese and the fat added in the shape of lard or "oleo oil" in adulterated cheeses.

<sup>\*</sup> Analysis and Adulteration of Foods, pp. 79 and 82.

	Water.	Fat.	Casein.	Non-nitro- genous and loss,	Ash.
Neufchâtel (Fleischmann) Emmenthaler (Fleischmann) Limburger (Fleischmann) Brie (Wynter Blyth) Camembert (Wynter Blyth) Parmesan (Wynter Blyth)	85.70 51.87	41.90 29,50 34,20 24.83 21.50 15.95	18.00 28.00 24.20 18,30 19.00 44,08	7.00 3.30 3.00 5.50 6.69	8.60 8.10 2.90 5.00 4.70 5.72

		100 P.	ARTS CO	NTAIN		of fat in of dry	of fat ts of d fat.	age in		NTAGI SITION E FAT
	Water,	Fat.	Casein.	Free acid as lactic.	Ash.	Proportion of 100 parts cheese.	Proportion of in 100 parts casein and f	Salt percentage in cheese.	Soluble acid.	Insoluble scid.
Stilton	28.57 28.63 81.55 32.26 81.85	39.13 38.24 35.93 34.38 34.34	82,55 29.64 28.88 27.16 27.88	1.24 0.27 1.32 1.35	3.51 8.49 8.42 4.88 4.58	51 19 53.57 52.49 50.75 49.02	52.50 54.12 53.34 54.24 53.08	0.67 0.72 0.82 3.04 2.11	4.42 4.26 4.81 4.91 4.40	88.91 89.01 88.41 88.71 89.11
Gruyère	85.60 83.66 87.11 85.75 41.30	31.57 30.69 30.68 28.35 22.78	. 28.16 30.67 26.98 31.10 28.25	0.45 0.27 0.86 0.81 0.57	4.22 4.71 4.42 4.49 7.10	46,26 48,78 48,78 44,12 38,80	50.49 47.02 50.84 45.24 42.41	1.48 0.81 1.69 1.28 4.45	4.55 4.41 5.55 6.68 5.84	88.78 88.91 87.76 86.81 87.51

Analyses of Oleomargarine and Lard Cheeses.

	1	00 Part	8 CONTAI	N			RTS OF ONTAIN	
	Water.	Fat.	Casein and free acids.	Ash.	Per cent. of salt.	Insol- uble acids.	Soluble acids.	Melting poin of fat.
Oleomargarine cheese Lard cheese	30.95 81.30	28.80 24.66	36.27 38.87	3.98 5.17	1.14 1.55	92,43 92,88	2.16 1.55	77° F. (25° C.) 92° F. (33.3° C

- 4. Milk-sugar.—The manufacture of crystallized milk-sugar (latose) has developed greatly in recent years, and a perfectly white, we crystallized product is now obtained. For its preparation, the swe skim-milk as it comes from the cream separator is precipitated wi acetic acid, filtered, and boiled either in open steam-heated evaporate or in vacuum pans. This first boiling should take several hours. To whey during the boiling becomes more cloudy, but suddenly clears, at the remaining albuminoids will separate in large flocks that can readic be filtered. It is to be filtered hot and boiled to crystallization in vacuum pan. The raw sugar so obtained can be refined and made which exactly as described under cane-sugar. As the first crystallization is a that can be brought to satisfactory color and purity, the yield is no much over ten per cent. of the total sugar contained in the milk.
- 5. Koumiss.—Koumiss is an alcoholic drink made by the ferment tion of milk. As made by the fermentation of mare's milk it has lor

been a favorite beverage with the Tartars and other Asiatic tribes. Cow's milk has been used chiefly in making it in both Europe and America. Mare's milk is the more suitable for fermentation because of the larger percentage of milk-sugar which it contains.

The fermentation is started by mixing fresh milk with some already soured. Both the lactic and the alcoholic fermentations are set up, with the production of lactic acid, alcohol, and carbonic acid gas. Some of the albuminoids are also changed into peptones. The composition of the koumiss as prepared from both mare's and cow's milk is shown in the accompanying analyses from various sources:

	Water.	Milk- sugar.	Lactic acid.	Albumi- noids.	Fat.	Alcohol.	Carbon dioxide,	Ash.
Koumiss from mare's milk (Fleischmann)	91.53 88.93 92.47 91.87 89.32	1.25 3.11 1.24 0.79 4.38	1.01 0.79 0.91 1.04 0.47	1.91 2.03 1.97 1.91 2.56	1.27 0 85 1.26 1.19 2.08	1.85 2.65 1.84 2.86 0.76	0.88 1.03 0.95 0.83	0.29 0.44 

6. Kephir.—This is a Caucasian product somewhat similar to koumiss, but prepared from cow's milk in leathern bottles by the aid of a peculiar ferment known as "kephir grains." According to Kern, as quoted by Allen (Commercial Organic Analysis, 2d ed., vol. iv, p. 242), the kephir ferment is an elastic cauliflower-like mass found below the snow line on certain bushes. The fungus consists of bacilli and yeast-cells, each cell containing two round spores, whence the name Dispora caucasina. When dried, the kephir fungus forms hard yellowish grains about the size of peas. By soaking these in water and adding them to milk, alcoholic fermentation ensues and the kephir is matured in a few days.

The following figures show the comparative percentage composition of fresh milk, kephir, and koumiss:

	Fresh Milk.	Kephir.	Koumiss.
Fat	8.8 4.8 4.1 Trace. None.	2.0 8.8 2.0 0.9 0.8	2.05 1.12 2.20 1.15 1.65
Water and salts	87.8	90.49	91.83

7. Casein Preparations.—Casein is now utilized on a large scale, first, as a basis of food preparations; second, as a fixing agent in calico printing instead of albumen; and third, as a substitute for glue in cements. For the first class of compounds, the casein salts of the alkalies and alkaline earths are used, and are obtained by dissolving casein in the calculated amount of caustic alkali, alkaline carbonate or phosphate or milk of lime, and evaporating the solution in vacuo. The products are dry white powders. For the second class of compounds, casein is gen-

erally dissolved in ammonia or in borax solution and used either with without formaldehyde. A very superior paper size is thus made which is used on glazed cardboard. A mixture of casein with slaked lime se to a hard insoluble mass, which is sometimes employed as a cement frearthenware and for similar purposes as a cheap substitute for glue.

In making these casein cements the most important point that is to noted to insure success is the freeing of the casein from all oily matter Therefore, when curd is prepared from milk, use only the most careful skimmed milk quite free from cream, such as separator skimmed mil When the casein has been separated and thoroughly washed it is ur formly mixed with quicklime and applied quickly. It then sets verapidly. Silicate of soda solution and borax are also used instead quick-lime, and form excellent cements with casein. Käseleim pulver, ready-made Swiss preparation, will set when moistened.

8. Whey.—The aqueous liquid remaining after the separation of the butter-fat and the casein, or curd, is termed the whey. Its more in portant constituent is milk-sugar, which in sour whey has been change in part into lactic acid. It also contains soluble nitrogenous constitutent such as milk-albumen and peptonized casein. On account of these constituents it is an easily digestible preparation and one assisting digestion. Hence the use of the "whey treatment" in medical practice for dyspeptics and those suffering from enfeebled digestion. The chief in portance, however, of the whey is for the extraction of the milk-sugation which has developed into an important article of manufacture. Oth products of minor and local importance only are "whey butter," "who alcohol," from which latter "whey champagne" is made, and "who vinegar." For the analysis of whey see p. 280.

# IV. Analytical Tests and Methods.

1. For Milk.—The specific gravity of milk is an indication of valu as it varies according to the content of fat, being higher for a skimme milk than for a whole milk. However, when the cream has been remove the specific gravity may be reduced to that of normal milk by the add tion of water, and then the specific gravity determination taken alor would be fallacious. Hence the detection of the adulteration of milk ! addition of water cannot be made with entire accuracy by the lactomet or specific gravity hydrometer in use. The lactometer officially used 1 milk inspectors in New York and other States indicates specific graviti between 1.000 (the specific gravity of water) and 1.038. gravity of 1.021 (taken as the minimum density of genuine milk) is al marked 100°, while the specific gravity of water (1.000) is called C Hence if the lactometer read 70°, the sample is supposed to conta seventy per cent. pure milk and thirty per cent. water. lactometric strength of about twenty thousand samples of milk examine by the New York State Dairy Commissioner in the year 1884 was 110 equivalent to a specific gravity of 1.0319. Another form of lactomet used abroad is the Quevenne-Müller instrument, which is graduated absolute specific gravity readings between the limits 1.014 and 1.042, ar

then the limits of pure milk (1.029 to 1.034) indicated, and degrees of dilution with water also indicated as the specific gravity sinks below this. The degree of adulteration of skimmed milk is also indicated on the instrument in the same way.

The total solids form an important element in the examination of milk. In some States the minimum percentage of total solids allowed in a milk is stated by law. (In Massachusetts thirteen per cent.; in New York and New Jersey twelve per cent.) To determine the water and total solids, five grammes of milk are placed in an accurately weighed flat-bottomed platinum dish of not less than five centimetres diameter and dried on a steam bath until constant weight is obtained. Fifteen to twenty grammes of pure dry sand may be previously placed in the dish to facilitate drying. Cool in desiccator and weigh rapidly to avoid absorption of moisture.

To determine the ash weigh about twenty grammes of milk in a weighed dish, add six cubic centimetres of nitric acid, evaporate to dryness and ignite at a temperature just below redness until the ash is free from carbon.

Both fat and moisture may be determined with one weighing of the sample in the Babcock asbestos method. A hollow cylinder of perforated sheet metal sixty millimetres long and twenty millimetres in diameter, closed at one end by a disk of the same material, is taken. This is filled loosely with from 1.5 to 2.5 grammes of freshly ignited woolly asbestos free from fine and brittle material, cooled in a desiccator, and weighed. Then introduce a weighed quantity of milk (between three and five grammes) and dry at the temperature of boiling water to constant weight to obtain the moisture by loss. Extract the residue now by the aid of anhydrous ether until all the fat is removed, evaporate the ether, dry the fat at the temperature of boiling water and weigh. The fat may also be determined by difference, drying the extracted cylinders at the temperature of boiling water.

The paper coil method of Adams is also often used. In this a coil of white blotting-paper (or thick filtering-paper) previously purified with ether and dried is made to soak up the milk to be analyzed from a weighed beaker or pipette. The paper coil is then dried in a hot-air oven and placed in a Soxhlet (see p. 86) or similar fat-extraction apparatus connected with an inverted condenser and the fat extracted by ether or petroleum-ether.

The total nitrogen is estimated by evaporating a weighed portion of milk to dryness and making a combustion of the residue with soda-lime or by the Kjeldahl method of conversion into ammonia compounds and distillation from an alkaline solution. Casein may be determined in fresh milk as follows: Place about ten grammes of milk in a beaker with about ninety cubic centimetres of water at 40° to 42° C., and add at once 1.5 cubic centimetres of a ten per cent. acetic acid solution. Stir with a glass rod and let stand from three to five minutes longer. Then decant on to the filter, wash first by decantation and then transfer the precipitate to the filter and complete the washing. The nitrogen is determined

in the washed precipitate and filter paper by the Kjeldahl method, usin 6.38 as the factor to calculate the easein.

The estimation of the milk-sugar by the polariscope is rendered dif cult by the presence in milk of various albuminoids, all of which tu the plane of polarization to the left, and the ordinary means of removi these albuminoids by a solution of basic acetate of lead is far from being perfect. Professor Wiley after extensive experiments upon this h adopted a method of optical analysis, using acid mercuric nitrate precipitate the albuminoids. He takes the specific rotatory power milk-sugar as  $(a)_d = 52.5$ . For details of his procedure the reader referred to Bulletin 107.\* Milk-sugar may also be determined eith volumetrically or gravimetrically with the aid of Fehling's solution (See p. 175.) In this case, it is also necessary to remove the albuminoid first, and this is done by Ritthausen's method of precipitation wi copper sulphate, all excess of this reagent being removed with caust potash solution. In calculating the results it will be remembered th the copper reducing power of milk-sugar is 70.5° as compared wi dextrose at 100°.

The sugar is probably most accurately determined by extraction fro the fat-free residue with weak boiling alcohol, filtering the alcohol fluid, and evaporating to dryness. This leaves the sugar with son mineral matter. On burning and determining this matter as ash the amount of sugar can be gotten.

The artificial coloring of milk is frequently practised to cover up the watering of the sample. The colors to be tested for are annatto, caram and anilin-orange, an azo-dye. Leach † has given the following schen for the detection of added colors in milk:

SUMMARY OF SCHEME FOR COLOR ANALYSIS.—Curdle one hundre and fifty cubic centimetres of milk in casserole with heat and acetic aci Gather the curd in one mass, pour off whey, or strain, if curd is finel divided. Macerate curd with ether in corked flask. Pour off ether.

## Ether Extract.

Evaporate off ether, treat with NaOH and pour on wetted filter. After the solution has passed through, wash off fat and dry filter, which if colored orange, indicates presence of annatto. (Confirm by SnCl<sub>2</sub>.)

#### Extracted Curd.

- (1) If colorless—indicates presence no foreign color other than in ether extract.
- (2) If orange or brownish—indicat presence of anilin orange or carame Shake curd in test-tube with concentrate hydrochloric acid.

If solution gradually turns blue, indicative of caramel. (Confirm by testing for caramel in whey of original milk.)

If orange cur im mediatel turns pink, in dicative of an lin orange.

The examination of milk for *preservatives* is constantly necessar. The most important of these preservatives is formaldehyde. To determine the constant of th

<sup>\*</sup> U. S. Dept. of Agricult., Bureau of Chem., Bulletin 107 (Revised), p. 118. † Food Inspection and Analysis, 2d ed., 1909, p. 177.

it according to Leach add ten cubic centimetres of commercial hydrochloric acid (specific gravity 1.2) containing two cubic centimetres of ten per cent. ferric chloride per litre to an equal volume of milk in a porcelain casserole and heat slowly over the free flame, giving the vessel a rotatory movement while heating to break up the curd. The presence of formaldehyde is indicated by a violet coloration varying in degree with the amount present. With fresh milk, one part of formaldehyde in 250 of milk may be thus detected.

Hehner's test may also be used. To five or ten cubic centimetres of milk in a wide test-tube add about half the volume of concentrated commercial sulphuric acid, pouring the acid carefully down the inside of the tube so that it forms a layer at the bottom without mixing with the milk. A violet zone at the junction of the liquids indicates formaldehyde. Benzoic, salicylic, and boric acids have also been used. The latter may be readily tested for by turmeric paper. Ten cubic centimetres of the milk are thoroughly mixed with six drops of concentrated hydrochloric acid. Turmeric paper moistened with this and dried will show a red color if boric acid were present in the milk.

2. For Butter.—The water in butter is determined by drying five grammes of the butter in a platinum dish at a temperature of 100° C. (212° F.) or slightly higher. The melted butter is stirred from time to time to facilitate the escape of the moisture. The water will have been given off in three to four hours, and it has been found that longer heating sometimes causes the melted fat to gain in weight.

To determine the salt, the dried butter just obtained is treated with warm ether or petroleum spirit, and the contents of the platinum dish poured on a weighed filter and washed with ether until all fat is removed. The residue and filter are dried and weighed. The salt is then dissolved out by warm water, and the chlorides in the solution estimated volumetrically by titration with decinormal silver nitrate, using a few drops of potassium chromate as indicator. The difference between the weight of salt ascertained and the total weight of curd and salt on the weighed filter is regarded as the amount of the casein, or curd, present. If after washing out the salt the residue on the weighed filter be dried and then weighed, the amount of casein so obtained is a little less than that gotten by difference. This is partly due to the small amount of milk-sugar washed out along with the salt and undetermined, and partly to the slight solvent action of warm water on some of the curd.

The percentage of fat may be obtained by evaporating the ether filtrate from the previous determination of salt and curd, but the butter-fat is liable to increase in weight by this treatment, and therefore the fat is usually gotten by difference after determining the water, casein, salt, and milk-sugar.

The adulteration of butter and the manufacture on a large scale of butter substitutes make an examination of the butter-fat one of great importance. This examination may be both qualitative and quantitative. The butter-fat is gotten for examination by melting a sample of butter and, after allowing the water and curd to settle, pouring the clear fat of to a dry warm ribbed filter and collecting the filtrate.

The specific gravity of the butter-fat may be taken, as first suggested by Bell, in a specific gravity bottle at a temperature of 100° F. (37.7 C.), or, as suggested by Estcourt and endorsed by Allen, with the aid the Westphal balance (see p. 87) at a temperature of 99° to 100° (210° to 212° F.). Bell found by this method that the specific gravity of true butter-fat varied from 909.4 to 914 (water 1000), while butter showed a specific gravity of 901.4 to 903.8. Allen gives the limit for pure butter-fat tested at 99° C. as 867 to 870, while butterine at the same temperature was 858.5 to 862.5.

The melting point of the butter-fat is also generally noted. Bell pr posed determining the melting point by first suddenly cooling son melted butter-fat by floating the capsule containing it upon ice-wate and then taking a fragment of the congealed butter upon the loop of platinum wire. This is then introduced close to the bulb of a the mometer in a beaker of water which is being heated from without. It the water becomes warmed the globule melts and the thermometer read off. An improvement on the method insuring greater accuracy recorded in Bulletin No. 107 (revised) of the Bureau of Chemistry, 133. The melting point of butter usually ranges between 29.5° C. ar 33° C. (85° to 90° F.), while the melting point of butterine is stated be between 25.5° C. and 28° C. (77.9° to 82.4° F.).

The quantitative examination of the supposed butter-fat may be made by several methods,—viz., the determination of the saponification equivalent by Koettstorfer's method,\* the determination of the percentage insoluble fatty acids present as glycerides by Hehner's method,† are the determination of the volatile fat acids after distillation by Reichert method.‡ To these most generally received methods may also be added the method of Hübl of iodine saturation as determining the character fatty acids, and the method of Morse and Burton, which combines to Koettstorfer and the Hehner processes, and determines the saponification equivalent of the soluble and the insoluble fat acids separately.

The term "saponification equivalent" is used to indicate the numb of grammes of an oil saponified by one equivalent in grammes of an alka Thus, tributyrin (the glyceride of butyric acid) has a saponification equivalent of 100.67, while tristearine (the glyceride of stearic acid) has a saponification equivalent of 296.67. Butter-fat, it will be remembere is a mixture of the several glycerides of the lower or volatile fatty acid and the higher or non-volatile fatty acids. Its saponification equivalent ranges from 241 to 253, the average being 247; butterine has a sapon fication equivalent ranging from 277 to 294, the average being 285.5. Hehner's method, the weighed quantity of the fat is saponified by alc holic potash, the soap solution evaporated down, taken up with water

<sup>\*</sup> Allen, Commercial Organic Analysis, 2d ed., vol. ii, p. 40.

<sup>†</sup> Bell. Analysis and Adulteration of Foods, Part ii, p. 56.

<sup>‡</sup> Allen, Commercial Organic Analysis, 2d ed., ii, p. 45.

and the fatty acids set free by an excess of hydrochloric acid. They are now brought upon a weighed filter, washed with boiling water until no longer acid, and then chilled into a cake by immersing the filter in cold water. The filter is then transferred to a weighed beaker-glass and the contents dried at 100° C. until constant in weight. The soluble fat acids can also be determined in this process by collecting the washings which were obtained with boiling water and making them up to one hundred cubic centimetres and then carefully titrating an aliquot portion with decinormal soda solution. This will give the amount of soluble fat acids plus the excess of standard hydrochloric acid used originally in liberating the fat acids. The amount of this excess can be ascertained by carrying through a blank experiment with alcoholic potash and hydrochloric acid, but without the fat. In the analysis of butter-fat the sum of the insoluble fatty acids and of the soluble fatty acids calculated as butyric acid should always amount to fully ninety-four per cent. of the fat taken. The soluble fatty acids calculated as butyric acid should amount to at least five per cent., any notably smaller proportion being due to adulteration. As an average, eighty-eight per cent. of insoluble and five and a half per cent. of soluble acids should be obtained.

While the true percentage of the volatile fatty acids cannot be easily obtained, the amount of alkali needed to neutralize them after distillation can be determined by Reichert's process. According to this, as improved by Meissl, five grammes of the fused and filtered fat are placed in a flask of about two hundred cubic centimetres contents with about two grammes solid caustic potash and fifty cubic centimetres of seventy per cent. alcohol, saponified on the water-bath and evaporated down until all alcohol is driven off. The thick soap-mass remaining is now dissolved in one hundred cubic centimetres of water, forty cubic centimetres of dilute sulphuric acid added, and, after adding a few fragments of pumice-stone, distilled with the aid of a Liebig condenser. About one hundred and ten cubic centimetres of distillate are collected, which requires about an hour. Filter and collect one hundred cubic centimetres in a graduated flask. Add phenol-phthalein as an indicator, and titrate with decinormal alkali. Increase the result by one-tenth, and reckon the result upon five grammes of the substance. It is found that two and a half grammes of butter-fat, examined by Reichert's method, require about thirteen cubic centimetres of the decinormal alkali, while butterine requires only one cubic centimetre. As the difference between these is twelve cubic centimetres, it may be calculated that there is 8.5 per cent. real butter-fat present in a mixture for every cubic centimetre of alkali required over the one cubic centimetre required for ordinary butterine.

Hübl's method is founded on the fact that the three series of fatty acids (acetic, acrylic, and tetrolic) unite in different proportions with the halogens, like chlorine, bromine, and iodine, to form addition products. The number of grammes of iodine absorbed is calculated to one hundred grammes of fat, and this is Hübl's "iodine number." Thus genuine butter has an iodine number from 30.5 to 43.0, while oleomargarine has from 50.9 to 54.9.

Morse and Burton \* saponify the combined fatty acids, liberate to free acids, wash out the soluble portion of the mixture, and then saponit again the soluble and the insoluble acids separately. They thus combine the Koettstorfer and the Hehner processes and get a greater certain as to the character of the fat mixture. Thus they find that with but 86.57 per cent. of potassium hydrate is required to neutralize the insoluble acids and 13.17 per cent. to neutralize the soluble acids, while with oleomargarine 95.40 per cent. of potassium hydrate is required for to insoluble acids and 4.57 per cent. for the soluble acids.

A physical test frequently applied to distinguish oleomargarine ar process (renovated) butter from true butter is the foam test. Tributter melted in a spoon over a free flame will foam abundantly, whi the other butter named will only burn and sputter like melted grease.

The presence of annatto coloring in butter is shown by treating tv or three grammes of the melted and filtered fat (freed from salt ar water) with warm dilute sodium hydroxide and after stirring pourir the warm mixture upon a wet filter. If annatto is present the paper we absorb the color so that when the fat is washed off by a gentle stream water the paper appears dyed straw yellow and on application of a droof stannous chloride solution turns pink.

For azo colors, melt a small amount in a test-tube and add an equ amount of a mixture of one part concentrated sulphuric acid and for parts glacial acetic acid and heat nearly to boiling, shaking the conten of the tube. Then set aside. The acid solution when settled will sho a wine-red color in the presence of azo colors.

3. For Cheese.—The methods employed in cheese analysis are most respects the same as those employed in the examination of butte. The fat is best extracted with light petroleum-ether, as common eth dissolves the free lactic acid as well as the fat. The remaining solid not fat can then be dried and weighed. The fat should be examined a Koettstorfer's saponification equivalent method, as the oleomargaria and lard cheeses may be detected in this way. Genuine cheese-fat, according to Muter, should not consume less than two hundred and twent milligrammes of potassium hydrate for each gramme used. If the chees should give unfavorable indications with Koettstorfer's test, then the soluble and insoluble fatty acids are determined in the fat according. Hehner. The percentage of insoluble fat acids in genuine cheese, according to Muter, averages 88.5, while in oleomargarine cheeses it is from 90.5 to 92 per cent.

The acidity, calculated as lactic acid, may be determined by treatin the residue from the fat determination with water and titrating the washings with decinormal soda solution. The washed residue then the non-fatty solids.

The ash is determined by ignition of the dried cheese before extration of the fat.

<sup>\*</sup> Amer. Chem. Journ., x, p. 322.

<sup>†</sup> Analyst, vol. x, p. 3.

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#### STATISTICS.

The only general statistics of the milk industry are those gathered for the Census Bureau in 1905, those for 1910 being not as yet avail-

able. The figures for the main products of the milk industry are follows:

	1905.	1900.	Increase.
Products, total value	\$168,182,789	\$130,783,349	\$37,399,400
Butter (lbs.)	531,478,141	420,126,546	111,351,595
Value	\$113,189,453	\$84,079,754	\$29,109,699
Cheese (lbs.)	317,144,872	281,972,324	35,172,548
Value	\$28,611,760	\$26,519,829	\$2,091,931
Condensed milk (lbs.)	308,485,182	186,921,787	121,563,395
Value	\$20,149,282	\$11,888,792	\$8,260,490
All other products	\$6,232,294	\$8,294,974	\$2,062,680
•			

(Report of Census Bureau, 1905.)

The oleomargarine production, as reported by the Internal Reven Bureau, has been:

	1909.	1910.
Uncolored oleomargarine (lbs.)	86,572,514	135,685,289
Colored oleomargarine (lbs.)	5,610,301	6,176,991
Total oleomargarine (lbs.)	92,282,815	141.862.282

The exportation of dairy products from the United States has d creased in recent years and was as follows:

:	1906.	1907.	1908.	1909.	1910.
Butter (lbs.) 27,3	60,537	12,544,777	6,463,061	5,981,265	3,140,5
Valued at \$4,9	22,913	\$2,429,489	\$1,407,962	\$1,268,210	\$785,7
Cheese (lbs.) 16,5	62,451	17,285,230	8,439,031	6,822,842	2,846,2
Valued at \$1,9	40,620	\$2,012,626	\$1,092,053	\$857,091	\$441,0
Oleomargarine (lbs.) . 11,7	94,174	5,397,609	2,938,175	2,889,058	3,418,6
Valued at \$1,0	33,256	\$520,406	\$299,746	\$293,746	\$349,9'
Oleo oil (lbs.)209,6	58,075	195,337,176	212,541,157	179,985,246	126,091,6
Valued at\$17,4	55,976	\$16,819,933	\$19,278,476	\$19,126,745	\$14,305,0
Condensed milk (lbs.)					13,311,3
Valued at \$1,8	89,690	\$2,191,111	\$2,455,186	\$1,375,104	\$1,023,6

Of miscellaneous products, there were produced in 1905, according to the Census Bureau, 1,161,414,457 pounds of skimmed milk valued \$1,368,738, and from this was extracted 11,581,874 pounds of caseing valued at \$554,099. The whey from which sugar of milk is obtained amounted to 166,451,226 pounds, valued at \$111,907.



#### CHAPTER VIII.

#### VEGETABLE TEXTILE FIBRES.

#### General Characters.

ALL the fibres which have been found of technical value for manufacturing purposes may be divided into the two great classes, vegetable fibres and animal fibres, the few found in the mineral kingdom among fibrous minerals being of relatively slight importance in textile manufacturing. Moreover, the distinction is not merely, as the name chosen would indicate, one of origin, but fundamental structural and chemical differences also exist and make themselves evident upon the slightest examination. The vegetable fibres are exclusively cell-growths of relatively simple structure, which during their life form integral parts of the plant organisms, while the animal fibres may be either a hardened secretion like silk or a more complicated cell-growth like wool, distinguished by its scale-like surface.

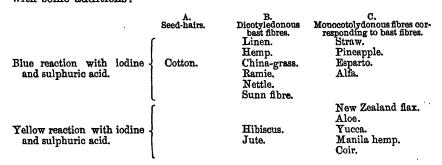
Thus the vegetable fibres are without exception some form of cellulose  $(C_6H_{10}O_5)_n$  in more or less pure condition or an alteration product of the same, while the animal fibres are composed of protein matter, and hence are nitrogenous.

The radical character of their chemical difference just referred to will be more thoroughly appreciated when we note the action of reagents upon the two classes respectively. The vegetable fibres are not dissolved or weakened by alkalies even at a boiling temperature, while the animal fibres are speedily disintegrated, with eventual liberation of ammonia from the nitrogenous material; on the other hand, sulphuric acid or hydrochloric acid rapidly causes a disintegration of the vegetable fibres by their action upon the cellulose, and nitric acid either oxidizes the cellulose or gives rise to nitrated derivatives, while the animal fibres are only slightly affected even when the acids are concentrated. These reactions will be referred to more fully in speaking of the analytical tests used for distinguishing the fibres in mixed goods. (See p. 353.)

The several vegetable fibres may be classified according to botanical or morphological character into three groups: (1) Seed-hairs (filaments composed of individual cells); (2) bast fibres (filaments or fibre-bundles made up of individual fibre-cells aggregated together); and (3) fibrovascular bundles. Sometimes the term bast fibres is made to include both the second and third classes as just given.

Chemically, all vegetable fibres are composed of cellulose. However, it has long been known that it is frequently more or less contaminated with altered products, which have been known as lignin, ligno-cellulose, adipo-cellulose, etc. The recent researches of Messrs. Cross and Bevan

have given us a clear understanding of the nature of the lignin and the alteration products of cellulose. The combination of cellulose and lignin, to which they apply the name of bastose, may make up the whole bundle of fibres, as in jute, or may be merely a covering upon the unaltered cellulose. By distinguishing between the cellulose and the bastose and mixtures of the two we may establish a chemical classification of the vegetable fibres. We are enabled to do this by the aid of the solutions of iodine (potassium iodide solution saturated with free iodine) and sulphuric acid (concentrated glycerine and strong sulphuric acid), which were first proposed by Vétillart.\* Pure cellulose when tested with the iodine and sulphuric acid solutions, one after the other, will give a pure blue color, while bastose shows under these conditions a yellow coloration. A complete classification, taking both botanical and chemical characters into account, is the following, which is that of Cross and Bevan's † with some additions:



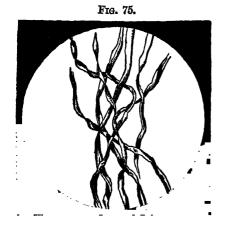
1. COTTON FIBRE.—The cotton, as already noted, is a seed-hair and envelops the seeds, which are at first enclosed in a capsule. With the ripening of the plant this capsule bursts and the contents spread out widely, consituting the cotton-boll, which is easily picked. The separation of the fibre from the enclosed seed is afterwards accomplished by the mechanical operation called "ginning," in which it is torn from the seed, so that while one end of an individual fibre is always closed the other is irregularly broken.

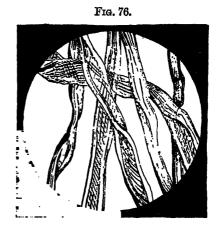
The genus Gossypium, to which all cotton-plants are referred, includes several well-marked varieties, the most important of which are G. Barbadense, or "sea-island cotton," grown off the coast of Georgia, South Carolina, and Florida, which yields the longest and strongest fibre or the finest "staple;" the G. hirsutum, or upland cotton, grown inland in Georgia, Alabama, Louisiana, and Mississippi, which yields a shorter staple; the G. herbaceum, grown in Egypt, Asia Minor, and India; the G. Barbadense, or "sea-island cotton," grown off the coast of Georgia, China and India and yielding the so-called "nankin" cotton of brown-yellow color; and the G. Peruvianum, yielding the long-stapled Brazilian and Peruvian cotton.

The structure of the cotton fibre is very characteristic. It presents a

<sup>\*</sup> Vétillart, Études sur les Fibres, Paris, 1876. † Text-book of Paper-Making, p. 46.

flattened and collapsed tube slightly twisted in spiral form, with comparatively thick walls and a small central opening. This structure is illustrated in Figs. 75 and 76, in the first of which the fibre is magnified thirty times and in the second of which it is magnified two hundred times. The first illustration shows the spiral twist of the fibres distinctly, but the collapsed character of the tube only slightly; this latter feature, however, is shown very distinctly in the second illustration. This flattening is not seen in the unripe fibre, which is a tube filled with liquid protoplasmic matter, but in the ripening of the plant this liquid dries up and the walls of the tube collapse and flatten out. The adhesion of the fibre to the seed also becomes less, so that the ripe cotton is easily separated in the ginning process. In some species (as in G. Barbadense) this separation of hair from the seed is so perfect that the seed shows





after the ginning a lustrous black appearance, whence the name locally applied of "black-seed cotton" as distinguished from the upland variety, known as "green-seed cotton."

The fibre must be picked when mature or it becomes "over-ripe" and deteriorates. The length of the "staple," or fibre, varies considerably with the different varieties of the cotton, the long-stapled sea-island cotton grown on the shores of Georgia and Florida attaining a length of nearly two inches (five centimetres), while the short native cotton of India scarcely exceeds three-quarters of an inch (eighteen millimetres) in length.\*

Chemically, the cotton fibre contains about ninety-one per cent. of pure cellulose, seven per cent. of moisture, and small amounts of fat, nitrogenous material, and cuticular substance. An ammoniacal solution of copper oxide causes the cellulose material of the fibre to soften and swell up, whereby the cuticle, which is not softened, takes the appearance of yellowish constricting rings binding the swollen cellulose at regular intervals. Prolonged action of the reagent dissolves the cellulose. When

<sup>\*</sup> Bowman, Structure of the Cotton Fibre, p. 19.

bleached by boiling with sodium carbonate or hydrate, the cuticle is decomposed and the fibre yields easily a very pure form of cellulose.

2. FLAX.—The flax-plant, Linum usitatissimum, yields the best known and probably the most valuable of the bast fibres as well as other products, like the linseed oil and linseed cake. (See p. 54.) It is not grown for both fibre and seed together, however, as when the fibre is desired in best condition the plant is gathered before it is fully matured, while if the plant is allowed to ripen fully for production of seed, the fibre obtained is more stiff and coarse.

The plant is grown through a wide range of climate, although that grown in the tropics, as in India, is chiefly used for seed, the fibre being of little value, while that grown in colder countries, as in the Russian East Sea provinces, yields the best fibre. When the plant is cultivated for the production of fibre, it is either sowed more thickly or, as in Hol-

land and Belgium, forced to grow up through a net-work of brushwood, thus yielding a more slender plant with a longer and finer fibre, known as *lin ramé*. The plant is not cut, but is always carefully pulled up by the roots, and the freshly pulled-up flax is at once submitted to the



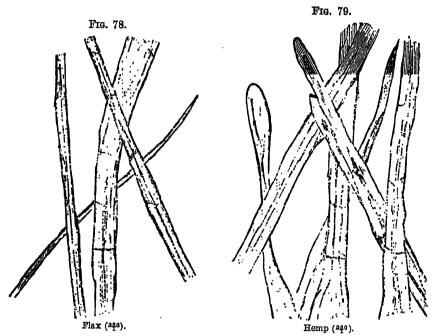
process of seeding, or "rippling," which is to remove the leaves and seed capsules. This is usually done by hand, drawing the bundles of the flax through upright metallic combs, or "ripples," the prongs of which easily catch the seed capsules, so that three or four drawings suffice to clean the stems or flax straws.

This straw, as it is termed, contains in a dried condition seventy-three or eighty per cent. of its weight of woody matter and encrusting material and twenty to twenty-seven per cent. of bast fibre.

The distinction between the several parts of the stem in the flax and similar plants yielding bast fibres is shown in Fig. 77 by both transverse and longitudinal cross-sections, where 1 represents the pith, 2 the woody tissue, 3 the cambium or partially lignified tissue, 4 the bast fibre, and 5 the crust or rind. To free these several parts of the stem from each other so as to obtain in a clean state the bast fibre is the object of the process of "retting." This is done either by natural means, as in the case of dew retting and cold-water retting, or by the help of an artificial process, as in warm-water retting and chemical retting. The dew retting, applied most largely in Russia, consists in leaving the flax thinly spread exposed to dew and rain, air and light, for eight or ten weeks, when, by the fermentation of the pectose matter of the rind, the bast fibre is thoroughly loosened. In cold-water retting either running or stagnant water may be used, the former being used in Belgium and the latter in Ireland. The bundles of flax are placed in crates and submerged, when actual fermentation ensues. The water must be soft, and care must be taken, especially in the stagnant-water method, to prevent

undue heating up during the fermentation. The warm-water retting requires a temperature of 30° to 35° C., and can be carried to completion in fifty to sixty hours, yielding an excellent product. The chemical process consists in the use of dilute sulphuric acid or hydrochloric acid, which allow of the completion of the process in a few days. After the retting process the flax is well washed and dried, and is then submitted to the mechanical processes of "breaking," "scutching," and "hackling" to thoroughly free the fibre from the woody layer and draw out the fibre-bundles into filaments.

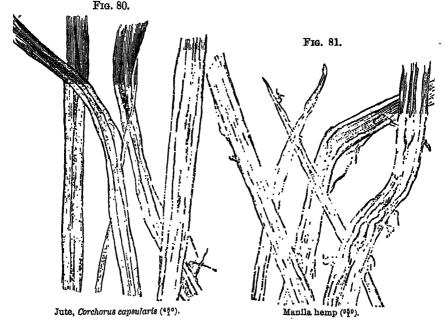
The flax fibre as seen under the microscope seems to be a long straight and transparent tube with thick walls and a minute central canal. Fig.



78 shows these characters of the flax fibre. Characteristic transverse markings also are shown, which may be nodal divisions or slight breaks or wrinkles produced by bending. Longitudinal fissures also show after vigorous rubbing. The linen fibre when cleansed has a blonde or even white color, a fine silky lustre, and great strength. It is less pliant and elastic than cotton, but is a better conductor of heat, and hence seems colder than cotton. Chemically it is, like cotton, a pure cellulose, but when swollen by the action of ammoniacal cupric oxide solution does not show the same uniform series of constricting bands of cuticle. Linen is in many respects more readily disintegrated than cotton, especially under the influence of caustic alkalies, calcium hydrate, and strong oxidizing agents like chlorine and hypochlorites.

3. Hemp.—The fibre known by this name is the product of the Cannabis sativa, which is grown for textile purposes chiefly in Russia and

Italy, while the seed is grown in India. It is a bast fibre similar to that of the flax-plant, but coarser, stronger, of deeper color and less lustre. Fig. 79 shows the microscopical characters of the hemp fibre. Its cultivation is very similar to that already described under flax, and differs according as the fibre or the seed are sought. The freshly-plucked hemp loses sixty per cent. of its weight in drying, and from the air-dried hemp straw twenty per cent. of bast fibre is obtained in the case of the male plant and twenty-two per cent. in the case of the female plant. It is used chiefly for ropes and cordage, and the fabric woven from it, known as canvas, is used in sail-making. Much of the finer fibre, however, is combined with linen fibre in weaving other goods. The iodine and sulphuric



acid test shows that the hemp fibre is not composed of pure cellulose, but is a mixture of cellulose and bastose.

4. Jute is the bast fibre of two species of the genus Corchorus, and is grown chiefly in India and Ceylon. The fibre is separated from the plant by methods similar to those employed with flax and hemp, the process of cold retting in stagnant water being followed generally. The bast fibres attain a length of 2.5 metres or even more, are of a yellowish-white color, and have a fine lustre. It is seen under the microscope to consist of bundles of stiff lustrous cylinders with walls of very irregular thickness. These characters of the jute are shown in Fig. 80. Chemically, jute differs from the bast fibres hitherto mentioned in that it contains no free cellulose, but consists of the chemical compound of cellulose with lignin, to which Cross and Bevan, who investigated it, gave the name of bastose. It gives, treated with iodine and sulphuric acid, a deep brown color. Moreover, the bastose acts with basic dye

colors, like the aniline dyes, as if it had been mordanted with tannin, and can therefore be dyed directly without previous treatment. It is much more easily affected by the action of acids and alkalies than flax or hemp. The influence of air and moisture will also rot the jute fibre. It cannot be bleached safely with chloride of lime because of the readiness with which the fibre is oxidized, but it may be bleached with a weak solution of sodium hypochlorite or by the successive action of potassium permanganate and sulphurous acid. It may be considered as showing more resemblance to the animal fibre in lustre and appearance than any of the other vegetable fibres, and is therefore frequently mixed with wool, mohair, and silk in certain classes of goods.

Among the fibres of lesser importance which serve as substitutes for hemp and jute are Manila hemp, Sunn hemp, and Sisal hemp. The first of these is a tropical fibre, obtained on the Philippine Islands from the leaves of the wild plantain. The fibre is obtained by cutting open the leaf-stalks, which are from six to nine feet in length, and then scraping them free from pulpy matter. It furnishes a very superior rope-making fibre because of its combined lightness and strength, and the finer grades are used for woven goods. The color is yellowish or white, and the white variety has a fine silky lustre. It is shown in Fig. 81.

The Sunn hemp is grown in India, and furnishes a fibre of light-yellowish color and resembles jute, although less lustrous. It is well adapated for cordage and netting.

Sisal hemp (or henequen) is derived from the fleshy leaves of a species of agave grown in Yucatan, British Honduras, and the West Indies and Bahamas. It is used largely in the United States as a substitute for jute in the manufacture of bagging and for cordage, being stronger and lighter than jute.

Ramie fibre (China-grass).—The bast fibre from two varieties of Boehmeria nivea, known in India as Rhea, in the Malay Archipelago as Ramie, and to Europeans as China-grass, has in recent years attracted very favorable attention from all interested in textile industries. seems to thrive best in the tropics and requires a great deal of moisture. The bast fibre cannot be removed from the woody stems by the retting process used for flax and hemp, as the intercellular substance is so easily decomposed that the water retting rapidly resolves the fibre into a magma of separated cells. The fibre must be removed from the woody stem while the plants are in the green state, as when dried, even by several hours' exposure to the sun, the fibre becomes difficult to remove from the woody portion. The length of the cells makes it possible to cut the ramie fibre into short lengths and to treat the cleansed fibre like cotton rather than like a long bast fibre. Hence the name "cottonized" ramie which has been applied to that exported from China. improved methods it is found possible to cleanse it in full lengths, and the fibre is worked like flax rather than with cotton-spinning machinery. The machines for breaking and decorticating the ramie are numerous. but few if any are entirely satisfactory. The properly-prepared fibre is of fine silky lustre, soft, and extraordinarily strong. It is undoubtedly the most perfect of all the vegetable fibres, and will play a great part in the industries of the future, especially as the plant, being a perennial, can be grown continuously for years, spreading of itself very rapidly and yielding several crops yearly. Its cultivation has been begun successfully in Louisiana and Mississippi, and it can probably be extended through the Southern States and Mexico, where is has also beer tried. The iodine and sulphuric acid test shows the ramie fibre to be composed of a pure cellulose, which swells easily and voluminously wher treated with ammoniacal solution of cupric oxide. The appearance of the China-grass is shown in Fig. 82.

Nettle Fibre.—The fibres of the common nettle (Urtica dioica) were at one time prior to the development of the cotton industry used extensively in spinning and weaving on the Continent of Europe, the cloth made being known as grass-cloth, the name now given to the product of the China-grass, or ramie. fibre when cleansed is soft, of good length and strength, and quite lustrous and white. The bast fibres of the linden (Tilia Europæa) and of the papermulberry - tree (Broussonetia papyrifera) are also used, the former for the manufacture of mats in Russia and the latter by the paper-makers of China and Japan.



New Zealand Flax is a fibre

obtained from the leaves of *Phormium tenax*, which acquires a lengt of one to two metres. The fibre as prepared by hand-scraping, the method of the native Maoris, is soft, white, and of silky lustre; as prepared by machinery it is distinctly inferior in character. Its chievalue is for rope-making and for coarse textiles. The rope made from this fibre is, however, weakened when wet by sea-water, and thereformust be kept well oiled.

Pineapple Fibre.—The leaves of the several varieties of Bromel yield a fine, nearly colorless, fibre, which is worked, especially in Braz for the manufacture of the so-called "silk-grass."

Esparto.—This is a grass, cultivated especially in North Africa ar Spain, where ropes and cordage are made from it. Its chief use, however, is in connection with paper-making. (See p. 313.)

Cocoa-nut Fibre (Coir).—The coarse fibrous covering of the nut the coco palm is largely used for brooms, brushes, matting, and coar

carpeting. The fibre is coarse, stiff, very elastic, round, and smooth like hair. It also has great tenacity, and is well adapted for cordage.

The classification of the vegetable fibres just enumerated has already been made upon the basis of the iodine and sulphuric acid reaction according to Vétillart. Two groups were thus established, the one composed essentially of unaltered cellulose and the other of lignified cellulose bastose. Other reactions of these two classes of materials are given in the accompanying table from O. Witt:\*

Reagent.	Cellulose.	Bastose (compound of cellulose with lignin).
Iodine and sulphuric acid. Sulphate of aniline with free sulphuric acid.	Produces blue color. Indifferent.	Produces a yellow or brown color. Colors deep yellow.
Busic aniline dyes. Weak oxidizing agents. Ammoniacal cupric oxide.	Indifferent. Indifferent. Immediate solution.	Produces fast colors. Rapid disintegration. Swelling up, blue color, and slow solution.

To distinguish the several more important vegetable fibres from each other when admixed, a number of chemical and physical tests have been proposed in addition to the microscopical study of the structural differences already mentioned under the individual fibres.

Thus, according to Kindt's test, the presence of cotton fibre in linen goods can be distinguished, after first removing the size or dressing by thorough boiling with distilled water and drying again, by dipping them from one-half to two minutes, according to the texture of the goods, in concentrated sulphuric acid. They are then well washed with water, rubbed, dipped for a moment in ammonia-water, and dried. The cotton fibre is either dissolved or gelatinized and removed by the rubbing, while the linen fibre remains unchanged or but slightly attacked. By counting the flax fibres remaining for a given superficial area the relative proportion of cotton admixture can be determined.

The different effect of strong caustic potash solution upon cotton and linen fibres is also taken as decisive at times, although the difference is not so marked. Both kinds of fibres shrink in size, the cotton fibres remain whitish or grayish yellow, while the linen fibres are colored deep yellow or orange.

A very characteristic test is that given by Boettger. A piece of the mixed goods frayed out in three sides is first dipped in a one per cent. solution of fuchsine, then taken out, washed in running water until this runs off clear, and dipped in ammonia-water for from one to three minutes. The cotton fibre is quickly decolorized, while the linen fibre remains bright rose-red in color. A test easily applied and satisfactory is the oil test, but it is only applicable to white goods which are free from size. The well-dried sample is dipped into olive oil, and then well pressed. The linen fibres become translucent from the capillary action upon the oil, while the cotton fibres remain white and dull in appearance.

<sup>\*</sup> Chem. Technologie der Gespinnstfasern, p. 111.

An alcoholic cochineal solution (one part of powdered dyestuff of gested with twenty parts of alcohol of .847 specific gravity for twent four hours) is also recommended by Bolley. Cotton fibres take a cleared color in this solution, while linen fibres are colored violet.

A special test to distinguish the fibre of the *Phormium tenax* (Ne Zealand flax) from linen or hemp is given by Vincent. It is in the u of concentrated nitric acid, which colors the New Zealand flax distinct red, but does not change the other fibres mentioned. (For tests to di tinguish the vegetable fibres as a class from the animal fibres, see p. 302

The use of the microscope, however, is much the most reliable mean of distinguishing the several fibres when occurring in admixtures, as the structural characters are sufficiently distinct to allow of easy recognition to those possessed of some practice.

# INDUSTRIES BASED UPON THE UTILIZATION OF VEGETABLE FIBRES.

The great utilization of these fibres is of course in the manufacture of textile fabrics of all grades. Having described the fibres which constitute the raw materials of these industries, we shall pass the mechanic side of their treatment and shall note the chemical processes of bleaching, dyeing, and color-printing in a later section of the work (see p. 522 after the preparation of natural and artificial dye-colors has been discribed. Other industries based upon utilization of some one or more of the vegetable fibres are Paper-making, Pyroxylin and Gun-cotton, Colodion, Celluloid, and most recent Artificial Silk.

## A. PAPER-MAKING.

#### I. Raw Materials.

1. Rags.—The first in order of use for paper-making and still the most important raw materials for the finer grades of paper are line and cotton rags. As the cellulose of these rags has already undergon a process of purifying from the coloring and incrusting matter wi which it was first associated in nature in its preparation for man facture into textile fabrics, it is well adapted for use in paper-makin the basis of which is also a cellulose fibre. Of course, the rags may l of all grades of cleanliness. They may be cuttings obtained in the cour of manufacture of garments, and being unworn may be relatively clea or they may be fragments of cast-off wearing apparel gathered fro waste-heaps and reeking with filth. Indeed, so great is the demand for paper-making stock that rags are gathered from Japan, Egypt, and a parts of the world, and the bales generally require careful disinfection before they can be used. They may contain sizing and China clay ar other loading materials, or they may be colored with various dyes ar metallic salts. Rags considered as paper-making stock must therefore assorted, and for trade purposes they are divided into a large numb of grades or classes distinguished by different letters.

Linen rags are distinctly superior for paper-making to cotton rags, as they make a stronger and more durable paper.

2. WOOD FIBRE.—Two varieties of pulp for paper-making may be obtained from wood,-viz., mechanically and chemically prepared pulp. Of these, the mechanical wood-pulp obtained by shredding the wood serves for the inferior grades of paper only, as its fibres are too short and do not "felt" or interlace sufficiently. It can therefore be used only as a filling material. Moreover, the resin present resists strongly the action of bleaching agents, and the paper becomes yellowish after This mechanical wood-pulp is known to the trade as "ground wood" and it is obtained by forcing the barked timber cut in short lengths against rapidly revolving stones or grinders, keeping a steady stream of water in contact with it to prevent the development of heat. This fibre, although, as said, very short, is used in enormous quantities to "fill in" in the manufacture of newspapers. No attempt is made to bleach it before making paper, it being merely necessary to incorporate in the stock sufficient coloring matter to overcome the yellowish tinge which otherwise would be evident. On the other hand, what is termed chemical wood-pulp has met with great favor as a very pure and easily obtainable form of cellulose. Chemical pulp is made by three distinct processes, known to the trade as the sulphite, soda, and sulphate proc-In all of these cases the timber is thoroughly denuded of bark and is then split and put through a "hog" or chipper which produces short, coarse heavy chips of about a half-cubic inch in volume. These are screened to obtain a fair degree of uniformity and separate the dust.

In the sulphite process, there are two methods of cooking, known as the "quick cook" and the "slow cook" or Mitscherlich method. former is now more extensively used by large manufacturers of newspaper and by book paper manufacturers to obtain their raw sulphite The cooking liquor is made from a dolomitic milk of lime saturated with sulphur dioxide, thus forming a mixture of magnesium and calcium bisulphite; or by another method high wooden towers are kept packed with lime-stone while water is allowed to pass down over the stone against a counter current of sulphur dioxide which displaces the carbon dioxide in the limestone. The digestors in most common use are about forty feet high, vertical, with conical bottom, and of boiler steel lined with rough or glazed firebrick set in an alkaline silicate The "cook" lasts six to eight hours, during which time a steam pressure of about 120 pounds is maintained, while the excess of sulphur dioxide developing is frequently allowed to pass off through relief pipes. The pulp when "blown" from the digestor is washed and if for book or writing paper is bleached with chloride of lime, or if for news, wrapping or bag paper is allowed to go to the beating engines unbleached.

In the case of the "slow cook" or Mitscherlich process, a horizontal cylindrical digestor is used having the same kind of lining as above described, but in which the heating is indirect by leaden steam coils placed longitudinally on the bottom inside the digestor. This "cook"

lasts about forty hours under a comparatively low pressure. Although the resulting material has had the lignin dissolved from it, it retains the original form of the uncooked chips and though soft must be ground before beating. Cross and Bevan explain the efficacy of the bisulphite processes by saying, "The chief agency is the hydrolytic action of sulphurous acid, aided by the conditions of high temperature and pressure; and the subsidiary agencies are, (1) the prevention of oxidation; (2) the removal from the sphere of action of the soluble products of resolution in combination with the sulphite as a double compound, for it is to the class of aldehydes that we have shown that the non-cellulosic constituents of wood belong; and (3) the removal of a portion of the constituents in combination with the base,—i.e., with expulsion of sulphurous acid."

At the present writing, the large consumption and rapidly diminishing supply of timber adapted to the sulphite process will cause a search for new fibres and an abandonment of the sulphite process in favor of the other chemical processes of treatment.

The soda process is used for the working of a variety of woods such as different kinds of long-leaf pine, spruce, hemlock, poplar, bass, etc. The cooking of the wood is comparatively simple. A vertical elyindrical welded digestor is used without any lining. The cooking liquor is generally a caustic soda solution testing about 12° B. The time of digestion is the same as in the "quick cook" sulphite process. The soda takes up the ligneous and resinous portion of the wood, and, when separated from the pulp, is evaporated, incinerated, and recausticized, with a loss of ten to fifteen per cent. in recovery, for cooking purposes. In this country, a large proportion of the soda pulp mills use poplar, spruce, and hemlock for the production of a fine grade of pulp for book paper. Others, using the long-leaf pine, produce a long, coarse fibre for wrapping paper.

The sulphate process, in large use in Sweden and Norway and to a small but increasing extent in the United States, produces what is known as a "kraft" pulp, which as the name denotes, has an extremely strong fibre and makes excellent wrapping paper. To obtain this, long-leaf pine is digested in soda digestors, and the process corresponds with the soda process except that before the incineration of the concentrated spent soda or "black liquor" sulphate of soda is introduced, which in the incineration causes the formation of a certain amount of sodium sulphide from the action of the carbon on the sulphate. This mixture of the caustic soda and sodium sulphide in cooking has the proper influence on the chemical changes taking place and produces long strong fibre.

- 3. ESPARTO.—This grass, mentioned under the vegetable fibres (see p. 309), is of great importance as a paper-making material, particularly in England. The Spanish variety, according to Hugo Müller, contains 48.25 per cent. and the African variety 45.80 per cent. of cellulose, but the yield of bleached fibre obtained in practice probably does not much exceed forty per cent. The fibre is tough and it makes an excellent paper, whether used singly or in admixture with other materials.
  - 4. STRAW.—As a material for admixing with other fibres, straw-

pulp is largely used. The varieties of straw so utilized are oat, wheat, rye, and barley. Of these, rye is the most suitable on account of its yielding the largest amount of fibre, and next in value is wheat. The amount of cellulose in winter rye is given by Hugo Müller as 47.69 per cent. and in winter wheat as 46.60 per cent., but probably not more than thirty-five per cent. is actually obtained as pulp, much being lost in the treatment on account of the loose aggregation of the cellular tissue. Straw contains more silica than Esparto, and hence requires more soda in the after-treatment to free the cellulose and adapt it for use.

- 5. Jute.—The "butts" or "cuttings" rejected by the textile manufacturer are largely used in the manufacture of the common grades of paper. It possesses a large percentage of cellulose (63.76 per cent. in the best fibre and 60.89 per cent. in the "butts"), but it cannot be economically bleached to a white color.
- 6. Manila Hemp.—This is very like jute in its adaptability for cheap and colored papers, and as the fibre is a lignified cellulose it requires considerable boiling with soda to prepare it for use.
- 7. Paper-mulberry.—In China and Japan, where the paper-makers excel the best European workmen in the making of some delicate but strong papers, the material chiefly used is the inner bark of the paper-mulberry-tree (Broussonetia papyrifera), the leaves of which can be used in feeding silk-worms. The strength of this paper is due to the fact that in making the pulp the long bast-cells are not broken and torn as in European pulping-machines, but merely softened and separated by beating. In taking up the pulp in the mould the cells are made to lie in one direction, and the paper may be strengthened by taking one or more dips in which the cells are made to lie in other directions. Some gum is added to make the cells of the pulp adhere.

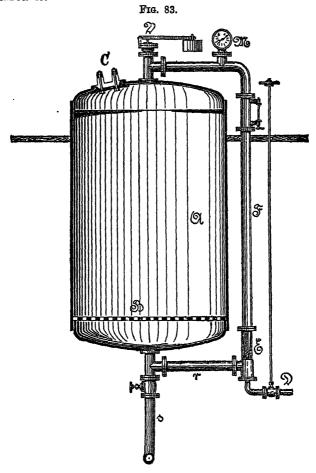
## II. Processes of Treatment.

1. MECHANICAL PREPARATION OF THE PAPER-MAKING MATERIAL.—
This differs, of course, according as the raw material is composed of rags or other cellulose-containing substance. With rags, a preliminary sorting always takes place, more or less complete according to the make-up of the bales. Numerous commercial designations are in use for these different grades so obtained. We need only speak of white linen, blue or gray linen, white cotton, colored linen or cotton, sacking, half wool, etc. They are then cut into coarse fragments by hand, being passed rapidly over broad knives fixed at a set angle in tables, and all buttons and hard substances removed. A thorough dusting or "thrashing" is now necessary to remove the dust and detachable dirt. This is effected in large wooden boxes with revolving arms. A more thorough cutting now ensues with the aid of revolving knives, followed in most cases by a final and thorough dusting, so as to eliminate as much dirt as possible and save in the amount of boiling necessary as the next operation.

With Esparto a mechanical sorting or "picking" is also the first operation. The grass is spread out on tables and the weeds, root-ends,

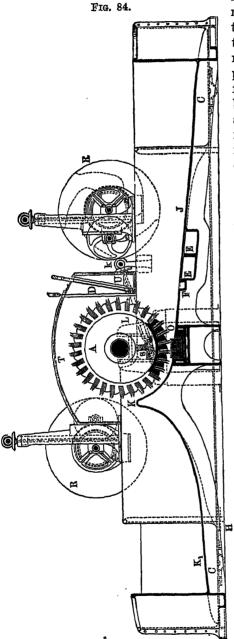
etc., carefully removed, as these would be difficult to boil and bleach as would give rise to dark-colored specks in the finished paper known "sheave." Machines for this cleansing of the Esparto are also use quite largely.

The preparation of mechanical and chemical wood-pulp has alread been referred to.



2. Boiling.—The boiling of the rags with caustic soda, caustic lim or a mixture of soda ash and lime, which is the next operation, designed to free them from grease, dirt, and coloring matter. This me be done either in rotating spherical or cylindrical boilers or in the so-called "vomiting" boilers described later. The boilers are often large enough to take two tons of rags at a charge. The amount of alka usually ranges from five to ten per cent. on the weight of the rage Soda is preferred by many paper-makers to lime on account of the greater solubility of the compounds it forms, although both are in general use. The time of boiling varies from two to six hours, according

the quality of rags, the alkali employed, and the pressure. The use of high pressure is to be avoided as far as possible, as it may result in



fixing the dirt and coloring matter instead of dissolving them. A pressure of from three to four atmospheres is commonly employed. After the pressure has been allowed to fall, the liquor collected at the bottom of the boiler is drawn off and the water run in to give the rags a slight preliminary washing. The charge is then drawn off.

In the case of Esparto, the "vomiting" boiler or other form of apparatus for keeping up a continuous circulation of the liquor is used. A form of boiler in which this circulation is kept up by the use of a steam injector is shown in Fig. 83. The grass is put in through the man-hole C and rests upon the false bottom B. Circulation is set up by the steam from the pipe D passing through the injector E and drawing the liquor through the small pipe r. In order that this circulation may proceed uniformly, it is necessary that the steam shall enter at a pressure one atmosphere higher than the pressure existing in the boiler. A manometer, M, shows the pressure, and a safety-valve, V, allows of the adjustment of the necessary conditions. The contents of the boiler are discharged through s at the end of the operation. The quantity of soda necessary depends upon the nature of the grass, Spanish requiring less than African, and the pressure

employed varies from five to forty-five pounds per square inch.

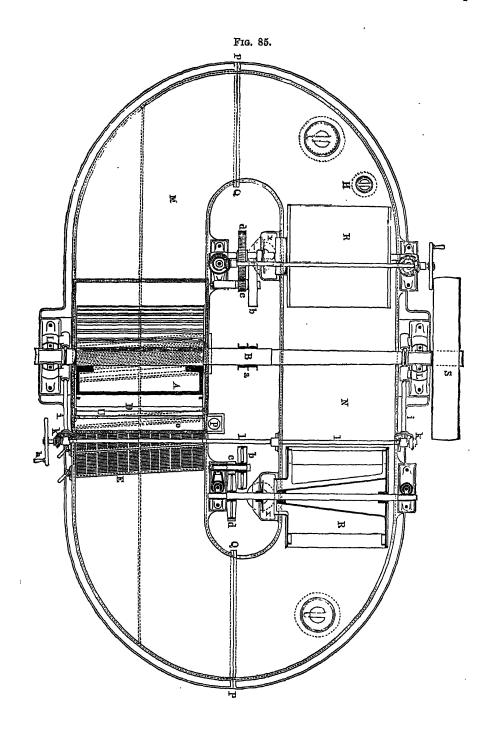
3. Washing.—This operation, which must be a thorough one, takes place in a washer or "breaker" The name "hollander" is war or

erally given to this machine as well as to the similar one in which th beating or mixing is done. The hollander is an oval iron tube, from te to twenty feet long, four to six broad, and about three feet high, divide for two-thirds or more of its length by an upright partition known a the "mid-feather." The details of its construction may be seen from Figs. 84 and 85. The roll A carries upon its circumference a number of steel knives and revolves on one side of the "mid-feather," or long tudinal division Q Q (Fig. 85). The floor on this side is raised in such way as to bring the pulp well under the roll, as shown by the line J O. (Fig. 84). Immediately under the roll is the "bed-plate," shown at ( and provided with knives similar to those in the roll A, but set wit their edges in the opposite direction. The distance between the roll an the bed-plate can be varied at will by means of the hand-wheel h an the mechanism shown at k and i (Fig. 85). After passing between the roll and the bed-plate, the pulp flows down the "back-fall" K K, an finds its way around to the other side of the mid-feather. On the in clined part of the floor and immediately in front of the bed-plate a sma depression is made at E, covered with an iron grating, for the purpose of catching buttons, small pieces of stone, and other foreign substance that may have found their way into the rags or other paper stock. dirty water from the rags is removed by the "drum-washers" R R. ends of the drums are of wood, and the circumference is covered wit fine copper or brass wire-cloth. The wash-water passes through the wir cloth into the compartment shown in R, and passing towards the na rower end of the inner conical tub, flows out through the side of the dru: into a trough placed to receive it.

In washing the rags in this machine, the tub is partly filled wit water, the rags from the boiler dumped in, and the operation begu. The action of the roll thoroughly mixes pulp and water and sweeps the rags up the incline and over the back-fall K. The dirty water the passes away through the drum-washer, the supply of pure water being so regulated as to keep the level constant. When the water begins run off clear the supply is stopped, the washer still being kept action. As the level falls, the drum is lowered by means of the handle When sufficiently drained, the pulp is discharged through the valv C C in the bottom of the washer. It is now ready to be bleached. The may be done in the washer itself or in separate engines called "potchers. If done in the washer, a solution of bleaching-powder is run in after the withdrawal of the wash-water and the action of the roll continue

Esparto is generally washed in exactly the same way as that ju described for rags, but in some mills the grass is washed in a seri of connected lixiviating tanks like those used in alkali-works. Pu water flows in at one end, passes through fresh lots of grass in succe sion, and issues at the farther end highly charged with the soluble pro ucts of the grass. The washed and broken pulp now goes by the nar of "half-stuff."

4. BLEACHING.—This is done with the aid of chlorine or a solution of calcium or sodium hypochlorite. The use of chlorine gas, once large practised, has been almost entirely superseded by the hypochlorite solution.



tions, as chlorine is liable to form difficultly removable compounds, and it also tends to attack and weaken the fibre of the pulp. When chlorine is used, 2.5 to 5 kilos. of salt are taken as needed for 100 kilos. of "half-stuff."

The solution of calcium hypochlorite must be used perfectly clear and free from undissolved hydroxide or carbonate. A solution of 6° Twaddle, which contains about half a pound of bleaching-powder to the gallon, is commonly used. An addition of hydrochloric or sulphuric acid to the bleaching-liquor is sometimes made, but this must be done with care so as not to liberate chlorine instead of hypochlorous acid. This danger from free chlorine is greater when highly lignified fibres, such as wood or jute, are used. The bleaching is often effected by combining a preliminary treatment in the "potcher" or washer with a subsequent prolonged steeping in tanks. A process has been recently proposed by Professor Lunge involving the use of acetic acid. The quantity required is very small, as during the process of bleaching it becomes regenerated. Any free lime in the solution is first nearly neutralized with a cheaper acid, such as hydrochloric or sulphuric acid, followed by the addition of the acetic acid. The process is said by Cross and Bevan to give excellent results with high-class material, such as the best cotton and linen rags, but is not to be recommended for materials like straw or Esparto.

A process invented by Thompson is also said to be very effective for the bleaching of rags. It consists in saturating the materials with a weak solution of bleaching-powder and then exposing them to the action of carbonic acid gas. The bleaching action is thus made very rapid and effective.

One of the most recent innovations in bleaching is the application of electricity in this connection. The earliest process that attracted much attention was that of M. Hermite. It is thus described by Cross and Bevan: \* "This process is based upon the electrolysis of a solution of magnesium chloride, this salt having been found to give the most economical results. The solution, at a strength of about 2.5 per cent. of the anhydrous salt (MgCl<sub>2</sub>), is electrolyzed until it contains the equivalent of about three grammes of chlorine per litre. This solution is then run into the 'potcher' containing the pulp to be bleached; a continuous stream is then kept up, the excess being removed by means of a drumwasher. This excess, which, after being in contact with the pulp in the engine, is more or less deprived of its bleaching properties, is then returned to the electrolyzing-vat, where it is again brought up to normal strength. It is claimed that the bleaching effect is much stronger than that of the corresponding amount of calcium hypochlorite solution. Moreover, the bleaching is much more rapid and the loss of weight which the substances undergo is less for equal degrees of whiteness obtained." In this country several successful electrolytic bleaching processes have been introduced in connection with the paper and pulp industry, such

<sup>\*</sup> Text-book of Paper-Making, p. 115.

as the Carmichael electrolytic process and the Whiting electrolytic process, both extensively used.

The removal of any excess of chlorine or bleaching-liquor must now be looked to. This is done either by careful washing or by the use of an "antichlor." The first method has the advantage of not only removing the bleach but also of the chloride of calcium which has been formed from it. It, however, takes some time and consumes a large amount of Much more general is the use of an "antichlor." The commonest of these is sodium thiosulphate (or hyposulphite, as it is commonly called). This is ordinarily decomposed according to the reaction  $2(Ca(ClO)_2) + Na_2S_2O_3 + H_2O = 2CaSO_4 + 2HCl + 2NaCl$ , but when the solutions are very dilute, sodium tetrathionate, Na2S4O6, and caustic soda and lime are formed. For the first equation two hundred and forty-eight parts of commercial thiosulphate are required to neutralize four hundred and nine parts of bleaching-powder of thirty-five per cent. available chlorine strength. The various sulphites are also in use as antichlors, sodium sulphite being the most important. A cheap antichlor is also made by boiling together lime and sulphur, the resultant calcium sulphide solution containing a mixture of calcium thiosulphate and calcium pentasulphide. This last-mentioned preparation is, however, objectionable on account of the free sulphur formed, as this affects the pulp injuriously. Whatever antichlor is used, an excess should be avoided, as it may act upon the color or size added subsequently. The antichlor should therefore be added in successive small portions, and any hypochlorite solution still remaining be tested for from time to time with iodide of starch paper, which will be turned blue as long as hypochlorite remains.

5. Beating.—The bleached pulp, or "half-stuff," is not yet in condition for making an even paper, as the fibre has not been sufficiently disintegrated. This is now effected in the beating-engine, which is a hollander very similar to the breaker already illustrated, except that the roll carries more knives and it is usually let down much nearer the bed-plate. The half-stuff is furnished in successive portions to the beater previously partially filled with water, each successive portion being allowed to mix thoroughly with the water before another lot is added. This is continued until the mass is so thick that it will only just turn round under the action of the roll. The operation of beating is designed to be a more complete breaking or tearing apart of the fibres rather than a cutting, as this latter result would interfere with the felting of the fibres so necessary in paper-making. Cotton and linen rags naturally take longer than most other paper-making material, taking often as much as ten hours; wood-pulp requires to be very gently and slowly. beaten, so that it requires some six hours; while Esparto is sufficiently disintegrated in from two to four hours. In making the finer grades of paper, the roller bars or knives instead of being made of steel are made of bronze, so that contamination with oxide of iron is avoided.

Beaters of a totally different form of construction are also largely in use. Thus, in the Jordan beater the roll is in the shape of a truncated

cone, fitted with knives and revolving in an iron box of corresponding shape, and also fitted with knives set at an angle. In the Kingsland engine and the Gould engine a circular plate furnished with kniverevolves against one or more stationary plates similarly fitted, somewhat after the manner of millstones. The half-stuff is even more thoroughly disintegrated in these beaters than in the ordinary forms.

6. Loading, Sizing, Coloring, etc.—Except in the very finest papers, some mineral loading material is incorporated with the pulp when in the beater. This is, of course, in the main for cheapening purposes, but also serves the useful purpose of filling the pores of the paper and enabling it to take a better surface in the subsequent operations of calendering. Such loading materials are China clay, or kaolin, sulphate of lime, or "pearl hardening," barium sulphate, precipitated chalk, bauxite, precipitated magnesia, and magnesium silicate, or "agalite." The amount added varies from two or three per cent. to twenty per cent., or in rare cases even more.

All papers except blotting-papers have also to be sized. This is for the purpose of filling the pores with some material that will, to some degree at least, resist the action of water. Thus, all writing-papers, and in general printing-papers also, are sized to prevent the ink applied to them from running. This is done either by what is termed "engine-sizing"—that is, in the beating-engine itself—or by "tub-sizing," when the paper as it goes through the Fourdrinier machine (see below) passes through a tub of gelatine size and takes a layer of the same on either surface.

In "engine-sizing" a rosin soap is first added to the pulp in the beater, and when this is thoroughly incorporated a solution of alum is run in, forming, as it has been generally supposed, a resinate of alumina which is water resistant when dried. Wurster \* claims to have shown however, that the sizing in this case is not due to the formation of a resinate of alumina but to a separation of free resin, and in this result he has been supported by Conradin.†

With the resin soap is also added some starch, and the quantity or mixed rosin and starch is usually from three to four pounds to the one

hundred pounds of pulp.

The pulp although bleached is rarely white enough to produce a clear white paper, and the yellowish tint requires to be neutralized by the addition of small quantities of blue and pink coloring material Ultramarine, smalt, and aniline-blue are used for the first color, and either cochineal, Brazil-wood, or aniline-red for the second. The paper may be colored throughout any desired color by using rags previously dyed, or by adding to the bleached pulp in the beater the necessary dye or pigments.

7. Manufacture of Paper from the Pulp.—We have to conside here two different products,—viz., hand-made paper and machine-mad paper. The former is made by taking in the mould upon the "deckel," or wire-cloth frame, just sufficient of the prepared pulp diluted with

<sup>\*</sup>Wagner's Jahresbericht, 1878, p. 1155. † Ibid., 1879, p. 1106.

water to make a sheet of paper. As the water drains through the wirecloth and leaves the fibres spread out upon the surface, the felting operation is assisted by shaking the frame gently from side to side. The mould with the sheet of paper is then turned over, and the sheet thus transferred from the wire to a piece of felt. When a number of sheets have been thus prepared, they are piled up with alternate sheets of felt and the whole subjected to strong pressure to expel water. They are then sized if required by dipping them into a solution of gelatine, again pressed, and hung up to dry. When dry they are calendered or pressed between hot metal rolls.

Machine-made paper is made on what is universally known as the Fourdrinier machine, of which an improved form, as manufactured by the Pusey and Jones Company, of Wilmington, Delaware, is shown in Fig. 86. We cannot here describe the various mechanical details of this machine, but may summarize by saying that it consists of an endless mould of wire-cloth on to which the prepared pulp flows from the "stuff-chest" through a "regulating-box" and over the "sand-table" and the "screen." From the deckel wire it now passes through a series of rolls, at first covered with felt and later of smooth heated metal known as the "dandy-roll," the "couch-rolls," the "press-rolls," the "drying cylinders," and, finally, the "calenders." The action of the machine is a continuous one, and the speed of the Fourdrinier is from sixty to two hundred and forty feet per minute,—the latter for cheap newspaper, the former for the best paper requiring the most care.

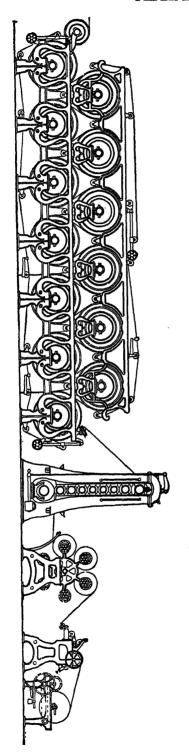
What is known as "tub-sizing" is applied to many machine-made papers in the course of their passage through the Fourdrinier. A filtered solution of gelatine is used to which about twenty per cent. of its weight of alum has been added. A certain quantity of soap is also often added, a white soap free from resin being used.

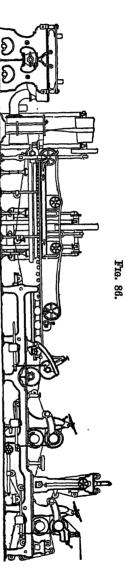
Instead of the Fourdrinier, what are termed cylinder-machines are also in use, in which a large drum or cylinder covered with wire-cloth revolves in the vat containing the pulp. As it revolves the fibres attach themselves to the wire and the water is sucked through the meshes by a partial vacuum within. The sheet of paper thus formed is taken on to an endless felt passing over a couch-roll, which revolves in contact with the hollow drum, and thence passes to a large drying cylinder heated by steam. Paper made on such a machine is weaker, however, than that made on the Fourdrinier, because it has not been found possible to give the shaking motion to the cylinder necessary to produce the felting of the fibres.

#### III. Products.

The products are almost without number, and vary not only in different countries, but even locally from time to time as different mills change their production. We will therefore attempt only a general classification of the main varieties.

1. BLOTTING- AND TISSUE-PAPER.—These are unsized papers. Blotting-paper is a mass of loosely-felted fibres, which, however, is free from





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any loading or filling material, and therefore is capable of easily and quickly taking up water or other liquids. It may be white, gray, or colored to any shade by the addition of the proper dyes. Tissue-papers, which as the name indicates are the thinnest of all papers, are made from very strong fibres, such as that of hemp-bagging and cotton canvas, and on machines somewhat different from the ordinary Fourdrinier.

- 2. Wrapping-papers.—These are partially-sized papers of coarse materials, such as straw, jute, Manila hemp, common rags, etc. They may show the natural color of the materials or may be colored, as in the case of the blue wrapping-paper commonly used for packing sugar. A more strongly sized and calendered wrapping-paper is made for use with linens and other textile goods.
- 3. Printing-papers.—These are white papers, generally with filling and sizing material, although some special grades are given a smooth surface by calendering instead of sizing. The cheaper grades for newspaper use are frequently largely adulterated with filling material, and mechanical wood-pulp is also largely used in their manufacture.
- 4. Writing-papers.—These are thoroughly-sized papers, for which the best materials are generally used, linen rags alone being taken for the finer grades.
- 5. CARDBOARD, PASTEBOARD, AND PAPIER-MACHÉ.—Pasteboard may be made by pressing a number of sheets of freshly-formed unsized paper in powerful presses, or cementing them together by the use of glue or other cementing material, and then pressing the mass so formed. Cardboard is made direct upon machines adapted for heavy layers of pulp and pressed and calendered like similar grades of ordinary paper. Papier-maché is made chiefly from old paper by boiling to a pulp with water, pressing, mixing with glue or starch paste, and then pressing in moulds previously oiled. After drying, the articles are soaked with linseed oil and then dried at higher temperature.

PARCHMENT-PAPER.—If a pure unsized paper be dipped in sulphuric acid of 60° B. a portion of the cellulose is changed into amyloid (hydrocellulose, according to Girard), which forms a gelatinous coating over the swollen fibres and effects in some degree a sizing of them. The paper is made hereby translucent and parchment-like, the strength is increased from three to fourfold, and the specific gravity by perhaps forty per cent. For the manufacture of this parchment-paper the long-fibred, unfilled paper is to be chosen. After treatment the paper is quickly washed, first with water, then with weak ammonia, and again with water.

In place of sulphuric acid we have the treatment with ammoniacal cuprous oxide solution or zinc chloride. The former reagent furnishes the Willesden ware, which always retains the light blue-green color; the latter yields the valuable product known as indurated or hard fibre. In preparing this latter material the paper, which is either unsized or prepared with a rosin size and then nearly dried, is dipped or run while in the roll through a bath of zinc chloride of about 65° to 70° B. kept at a temperature of about 38° C. After passing through the zinc chloride bath, the paper is passed over hot rolls and then cooled and washed

then dried in a heated room, given a coating of paraffin oil, and cale dered. The material so obtained is very strong, tough, and can washed.

6. Side-products.—Recovered Soda.—The alkaline liquors in which rags, esparto, and other paper-making material have been boiled were one time run off as waste products. This is no longer done in proper conducted mills, as the alkali used can be recovered in the form carbonate by evaporation of the waste-liquor and ignition of the residue and this carbonate can then be causticized and fitted for renewed us The soda during the process of boiling with the paper-making materia takes up a large amount of non-cellulose fibre constituents, such resin, coloring matter, and silica. These on evaporation and ignitic become either carbonate or silicate. It will not be possible for us he to describe the forms of evaporators in use for this soda recovery. Or of the best-known evaporators is that of Porion, used largely in En land on the Continent. For a description of this and other form see Cross and Bevan's "Text-book of Paper-Making," p. 182. In th country the Swenson form of evaporator has been largely used for tl "black liquor" of the soda pulp works.

The recovered soda consists essentially of carbonate of soda, togeth with a certain amount of silicate of soda if the liquor had been obtaine by boiling straw or esparto. The causticizing is done in the usual wa with caustic lime and the clear alkali decanted from the separated ca cium carbonate, which is then thoroughly washed.

# IV. Analytical Tests and Methods.

1. DETERMINATION OF THE NATURE OF THE FIBRE.—This may be do: in part, if not wholly, by either of two methods,-viz., by the aid of tl microscope or by the use of chemical tests for individuals fibres. The fibre is always torn or cut and often somewhat attacked. By some pra tice, however, it is possible to distinguish between cotton and linen to identify both in admixture. Wood and straw can also be identifie In making these tests, it is best to take strips of the paper in questic and boil them in succession with alcoholic potash solution, with wate with two per cent, hydrochloric acid, and then again with water. they are now shaken up with a little warm water, we obtain a fine magn of fibres, which when mixed with an equal volume of glycerine is we adapted for examination under the microscope. The distinctive cha acters of some of the chief paper-making materials as seen under tl microscope may be thus summarized, according to Cross and Bevan: Cotton,—flat, ribbon-like fibres, frequently twisted upon themselve The ends generally appear laminated. Linen,—cylindrical fibres, similar to the typical bast fibre. The ends are frequently drawn out into nume ous fibrillæ. Esparto,-the pulp consists of a complex of bast fibres ar epidermal cells. The most characteristic feature of esparto pulp is the presence of a number of fine hairs which line the inner surface of tl leaf, some of which still remain after the boiling and washing processe The presence of these hairs may be taken as conclusive evidence of the presence of esparto. Straw,—this closely resembles esparto pulp in microscopical features, except that the hairs are absent. On the other hand, a number of flat oval cells are always present in paper made from straw. Chemical wood-pulp,—flat ribbon-like fibres, showing unbroken ends. The presence of pitted vessels is eminently characteristic of pulp prepared from pine-wood. Mechanical wood-pulp may be recognized by the peculiar configuration of the torn ends of the fibres and from the fact that the fibres are rarely separated, but generally more or less agglomerated. The pitted vessels of pine-wood also show, and usually more distinctly than in chemical wood-pulp.

The chemical reagent most useful in testing paper-pulp is aniline sulphate. With most of the fibres which consist of cellulose simply it gives no reaction. Straw, esparto, and mechanical wood-pulp can, however, be identified by its means. Thus, where paper containing straw or esparto is treated for some time with a boiling one per cent. solution of aniline sulphate, a pink color is produced. Esparto gives the reaction with greater intensity than straw. Mechanical wood-pulp treated with this solution develops even in the cold a deep-yellow color. According to Bolley,\* the moistening of paper containing mechanical wood-pulp with nitric acid will give the same result, and a naphthylamine salt produces a deeper orange color. According to Wiesner, phloroglucin is also a delicate reagent for wood fibre in paper. A drop of dilute solution of phloroglucin put upon the paper and this followed by moistening with hydrochloric acid develops an intensely red color. Fuchsine also colors wood fibre red, but has no effect upon paper from linen fibre alone.

M. Wurster in "Journ. de Pharm. et Chemie" has extended Wiesner's observation on phloroglucin to a number of the phenols, finding them as a class to serve as reagents for distinguishing between woodpulp and other cellulose. The results are:

Reagent.	Wood-pulp. Dark red.	Cellulose paper. No color.
Resorcin	. Deep green.	Violet.
Pyrogallol		Violet.
Phenol	. Yellow-green.	Violet.
Phloroglucin		No color.

According to Godeffroy and Coulon, mechanical wood-pulp from pine-wood possesses the property, after it has been extracted with water, alcohol, and ether, of reducing gold solutions on boiling. This property is not possessed by wood-pulp prepared by the caustic soda or sulphite processes, after similar extraction with solvents, nor by the pulp prepared from linen or cotton fibres. This property depends upon the fact that in mechanical wood-pulp ligno-cellulose remains, and to this composition is due the reducing power upon gold solutions. This lignocellulose is destroyed in the preparation of chemical wood-pulp, and does not exist at all in the linen or cotton fibre. It has been found that on the average one hundred parts of mechanical wood-pulp, extracted with

<sup>\*</sup> Handbuch der Technisch-Chem. Untersuchungen, 6te Auf., p. 1006.

solvents and dried at 100° C., will reduce fourteen thousand two hundred and eighty-five grammes of gold. It is thus made possible by weighing the reduced gold to estimate the amount of mechanical wood entering into the composition of the paper. For details of the analytical method based upon this gold reaction, see Bolley's "Handbuch der Technisch-Chem. Unterschungen," 6te Auf., p. 1007.

- 2. Determination of the Nature of Loading Materials.—The total amount of the mineral loading material is determined by igniting a weighed quantity of the paper until the ash is white or grayish and then accurately weighing this. The ash from a paper containing the China clay is insoluble in boiling dilute hydrochloric acid; that from paper containing calcium sulphate is soluble, and deposits on standing needle-shaped crystals of gypsum easily recognizable by chemical tests.
- 3. DETERMINATION AS TO NATURE OF THE SIZING MATERIALS.—The iodine test serves to indicate the use of starch in the size, as it produces the well-known blue color. Extraction of the paper with alcohol containing a few drops of acetic acid serves to show the resin used in the The alcohol, after cooling, is poured into four or five times its bulk of water, when the resin separates, producing cloudiness or turbidity. Or, after extraction, the alcohol is evaporated, leaving the resin capable of being identified by its properties. Notable quantities of alumina in the ash also point to the use of resinate of alumina as sizing material. According to Wurster, if between two sheets of paper which have been sized with resin is pressed paper moistened with tetramethylparaphenylen-diamine solution, a bluish-violet color is produced, while paper free from resin is not affected. Boiling of the paper sample with distilled water, filtering, and adding a few drops of tannic acid solution will serve to show the presence of gelatine sizing. If present, a white curdy precipitate is formed on the addition of the tannic acid.
- 4. Determination of the Nature of the Coloring Material.—In deciding as to the presence of coloring matter, we must bear in mind the reactions of the commoner pigments used. Ultramarine is destroyed and decolorized on addition of acids; Prussian blue is decolorized by heating with alkalies; indigo is decomposed by heating with chlorine or nitric acid; smalt withstands the action of both acids and alkalies and remains in the ash as a blue glass; the aniline colors are capable of extraction with alcohol as solvent.

# B. GUN-COTTON, PYROXYLINE, COLLODION AND CELLULOID.

#### I. Raw Materials.

The basis of these preparations is the class of nitrates formed from cellulose by the action of nitric acid, either taken singly or admixed with strong sulphuric acid, or as developed by the action of sulphuric acid upon a nitrate. Using the doubled formula  $C_{12}H_{20}O_{10}$ , we may note the following five stages of nitration:

Hexanitrate, C<sub>12</sub>H<sub>14</sub>O<sub>4</sub>(NO<sub>3</sub>)<sub>6</sub> (trinitro-cellulose, C<sub>6</sub>H<sub>7</sub>(NO<sub>2</sub>)<sub>3</sub>O<sub>5</sub>, of other writers), is the true gun-cotton. It is formed by the action of a

mixture of the strongest nitric acid (specific gravity 1.52) with two or three parts of concentrated sulphuric acid, in which the cotton is immersed for twenty-four hours at a temperature not exceeding 10° C. (56° F.). The hexanitrate so prepared is insoluble in alcohol, ether, or a mixture of both, in glacial acetic acid, or in methyl alcohol. Acetone dissolves it very slowly. According to Eder, mixtures of nitre and sulphuric acid do not give this nitrate. It contains 14.14 per cent. nitrogen.

Pentanitrate, C<sub>12</sub>H<sub>15</sub>O<sub>5</sub>(NO<sub>3</sub>)<sub>5</sub>. It is difficult, if not impossible, to prepare this nitrate in a state of purity by the direct action of the acid upon cellulose. The best method (that of Eder) is to dissolve gun-cotton (hexanitrate) in nitric acid at about 80° to 90° C. (176° to 194° F.) and then precipitate as pentanitrate by concentrated sulphuric acid after cooling to 0° C.; after mixing with a larger volume of water and washing the precipitate with water and then with alcohol, it is dissolved in ether-alcohol and again precipitated with water, when it is obtained pure. This nitrate is insoluble in alcohol, but dissolves readily in etheralcohol and slightly in acetic acid. It contains 12.75 per cent. nitrogen. Strong potash solution converts this nitrate into the dinitrate.

The tetranitrate and trinitrate (collodion pyroxyline) are generally formed together when cellulose is treated with a more dilute nitric acid and at a higher temperature and for a much shorter time (thirteen to twenty minutes) than in the formation of the hexanitrate. It is not possible to separate them, as they are soluble to the same extent in ether-alcohol, acetic ether, acetic acid, or wood-spirit. On treatment with concentrated nitric acid and sulphuric acids, both the tri- and tetranitrates are converted into pentanitrate and hexanitrate. Potash and ammonia convert them into dinitrate.

The dinitrate,  $C_{12}H_{18}O_8(NO_3)_2$ , always results as the final product of the action of alkalies on the other nitrates, and also from the action of hot, somewhat dilute nitric acid upon cellulose. The dinitrate is very soluble in ether-alcohol, acetic ether, and in absolute alcohol.

The chief raw material for the manufacture of these nitrates at present is the waste from cotton-spinning, which has already been freed from the impurities of the raw cotton. It is first picked clean by hand from admixture with foreign matter and then torn and opened up by machinery so as to fit it for easy action of the nitrating acids. It is then treated for a few minutes with boiling potash solution, thoroughly washed, and dried by steam. For the manufacture of celluloid a specially prepared and perfectly pure tissue-paper is now used, which is torn into shreds by machinery preparatory to the nitrating.

#### II. Processes of Manufacture.

1. Gun-cotton.—The following is the procedure at Waltham Abbey, where gun-cotton is made for the English government under Sir F. Abel's improved method. A mixture of fifty-five parts of nitric acid (1.516 specific gravity) and one hundred and sixty-five parts of sulphuric acid (1.842 specific gravity) is taken for one part of cotton. The

nitrating mixture is placed in cast-iron vessels, cooled from without by flowing water, and the cotton immersed. It may either remain in these until ready for washing, or may after a brief immersion be transferred to smaller stone-ware vessels, similarly cooled, in which it then remains for twenty-four hours, for the double purpose of completing the nitration, so that the product shall contain a maximum of the highest, or hexanitrate, and of allowing the contents of the jar to cool down per-The nitrated cotton is then centrifugated, stirred up thoroughly with cold water, again centrifugated, and then washed systematically with warm water to which some soda has been added. gun-cotton so obtained may either be used in the loose form or, when designed for manufacture into cartridges, is beaten in a hollander after the manner of paper-pulp, and then washed and pressed in the desired The gun-cotton when finished is usually preserved in a moist state, and dried only when needed for use. It, however, does not require to be sharply dried, as with fifteen to twenty per cent. of moisture it can be made to develop its full explosive powers.

2. Pyroxyline and Collodion.—Pyroxyline of various grades of solubility can be prepared according to the strength of acids used and length of immersion given the cotton. In general, the nitric acid taken is less concentrated than that used for making gun-cotton, and a somewhat higher temperature is employed. Potassium or sodium nitrate is also used along with the sulphuric acid as the nitrating mixture, as the presence of nitrous acid in the nitric acid generated is considered as playing some part in the result. A mixture of twenty parts pulverized potassium nitrate with thirty-one parts of sulphuric acid of 1.835 specific gravity is given as a suitable pyroxyline mixture. After the nitre has entirely dissolved in the sulphuric acid and the mixture has fallen in temperature somewhat below 50° C. the cotton is put in, stirred around thoroughly, and then the vessel left covered for twentyfour hours at a temperature of from 28° to 30° C. The pyroxyline is then washed with cold water until it shows no acid reaction, and finally with boiling water to remove the last traces of potassium sulphate. A similar mixture, using sodium nitrate, is thirty-three parts of sulphuric acid of 1.80 specific gravity, seventeen parts of sodium nitrate. and one-half part cotton.

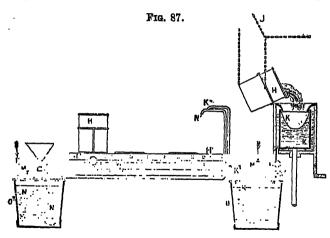
A special grade of pyroxyline for the manufacture of collodion, put upon the market by the Schering factory in Berlin, is made by immersing cotton for fifteen minutes in a mixture of equal volumes of sulphuric acid of 1.845 specific gravity and nitric acid of 1.40 specific gravity, taken at a temperature of 80° C.

The pyroxyline made from tissue-paper for the celluloid manufacturers is made by taking fifty cubic centimetres of nitric acid of 1.47 specific gravity, one hundred cubic centimetres nitric acid of 1.36 specific gravity, and one hundred cubic centimetres of sulphuric acid of 1.84 specific gravity. In this mixture eighteen grammes of the finely-shredded tissue-paper are immersed at a temperature of 55° C. for one hour. The paper gains about forty per cent. in weight in the nitration.

The method of carrying out this nitration as proposed by Hyatt, the

patentee of celluloid, is shown in the annexed illustration. (See Fig. 87.) The shredded paper is filled into the container H, in which has been placed a mixture of strong sulphuric and nitric acids heated to from 26° to 32° C. The mixture having been vigorously stirred by a mechanical stirrer which can be raised and lowered at will, it is allowed to remain at rest for twenty minutes to allow of the completion of the nitration. It is then swung around on the revolving table  $H^1$ , caught by a crane from above, and emptied into the centrifugal K, which quickly drains off the excess of acid from the mass, the liquid flowing through the pipe  $K^1$  into the reservoir  $O^1$ . The container H can be filled from this reservoir through the pipe  $K^3$  by the application of air pressure at M, as the lid of the acid reservoir is fitted on air-tight.  $O^2$  is a reservoir for fresh acid mixture.

The proportions of ether and alcohol used in dissolving pyroxyline to make collodion solutions vary very greatly. The United States Pharmacopæia prescribes for four grammes of pyroxyline seventy-five cubic



centimetres of ether and twenty-five cubic centimetres of alcohol; the British Pharmacopæia takes for one ounce of pyroxyline thirty-six fluid-ounces of ether and twelve fluidounces of rectified spirit; the German Pharmacopæia takes one part of pyroxyline to twenty-one parts of ether and three parts of alcohol.

3. CELLULOID.—The conversion of pyroxyline into celluloid is accomplished by effecting a thorough incorporation with the former of a certain amount of camphor. This may, however, be done in a number of ways, several of which have been carried out in practice. First, it is possible to effect it by heat alone, without the use of any solvent for either the camphor or the pyroxyline. The camphor at the temperature of its fusion becomes a sufficient solvent for the pyroxyline to effect complete physical admixture. This process is essentially that used in this country. The weighed amount of camphor is added to the pyroxyline while the latter is still in a partially moist condition, some alcohol sprinkled upon the mixture to aid in the comminution of the camphor,

mixture may now be put through heated rolls to effect the melting the camphor and cause it to penetrate and take up the pyroxyline every part of the mass. It is then put through a heated masticating machine to complete the admixing and make the mass of uniform conposition throughout. Coloring matter is added when desired to to materials before the camphor takes up the pyroxyline, so that it make thoroughly distributed or dissolved as the case may be.

A solution of camphor in either ethyl or methyl alcohol has also be used as the means of converting the pyroxyline into celluloid. The may be either with the aid of heat or, if sufficient of the solvent be use it may be carried out at ordinary temperatures.

A solution of camphor in ether has also been used in the cellulo factory of Magnus & Co. in Berlin. For fifty parts of pyroxyline a taken twenty-five parts of camphor dissolved in one hundred parts ether to which five parts of alcohol have been added. The mixture covered up and stirred from time to time. A gelatinous and glutino mass results, which must be rolled between calender rolls until acquires plastic characters. The process is distinctly more dangero than the others mentioned, as the ether is all allowed to evaporate, ar it does not yield anything better in the way of product.

#### III. Products.

1. Gun-cotton.—The explosive variety of gun-cotton, whether in the form of loose fibre or as compressed cartridge or paper sheets, cannot be readily told by outward characteristics from untreated cotton. On clo examination a slight yellowish tint is recognizable; it is slightly rough to the touch, and crinkles slightly when pressed; when rubbed it is easi electrified and sticks to the fingers. When lighted it burns quick without smouldering or leaving any residue. When heated slowly begins to decompose with evolution of acid fumes, and above 130° C. explodes. It is therefore necessary to exercise great care in the dryin of it, and especially if all traces of acid have not been removed. It much safer when wet than dry, although it is possible to explode it by co cussion when it still contains from fifteen to twenty per cent. of water

The explosive variety of nitrocellulose is a mixed penta- and hex nitrate and contains from 12.6 to 13.4 per cent. of nitrogen.

Gun-cotton is insoluble in water, alcohol, ether, chloroform, ar acetic acid, in dilute acids and alkalies. It is somewhat soluble in ac tone and wood-spirit.

Gun-cotton is chiefly used in submarine mines and blasting and fanaval torpedoes. The combination of it with nitro-glycerine, known blasting gelatine, has been referred to under another section. (See p. 85)

2. Pyroxyline.—This in most physical characters resembles pe feetly the explosive gun-cotton. The most important difference is the ready solubility of this variety of cellulose nitrate in a mixture of alcoholound ether, in which the higher nitrate is insoluble. The ordinary pyrologies, moreover, only slightly explosive. When dissolved in the strength noted before (see preceding page) we obtain,—

- 3. COLLODION.—This is a colorless liquid, which rapidly evaporates on exposure to the air, leaving a transparent film of tetranitrate, or tetra- and trinitrate mixed, insoluble in water and alcohol. It is used as a dressing for wounds under the name of "liquid adhesive plaster," and very largely in photography as a means of covering the photographic plates with a transparent film which shall hold finely divided and distributed the sensitive silver salt.
- 4. Pyroxyline Varnishes.—In recent years a very important class of metal varnishes or lacquers have been introduced under trade-names, such as Zapon varnish, etc., in which pyroxyline is the basis. This is dissolved in either methyl alcohol, acetone, methyl and amyl acetates, or mixtures of these. Petroleum-naphtha is also added to these solvents to facilitate the drying. These varnishes are of special value for fine metal-work in brass or bronze, as they leave a perfectly transparent and flexible film of pyroxyline, which protects the metal and will not crack or peel when properly applied.
- 5. CELLULOID.—This valuable product of the action of camphor upon pyroxyline is prepared under a great variety of forms, both transparent and opaque, colored uniformly, or mottled and striated in imitation of ivory, coral, amber, tortoise-shell, agate, and other substances. It cannot be caused to explode by heat, friction, or percussion. When brought in contact with flame it burns with a rustling flame, and continues to smoulder after the flame is extinguished, the camphor being distilled off with production of thick smoke, while the nitro-cellulose undergoes incomplete combustion.

Celluloid dissolves in warm, moderately concentrated sulphuric acid, but is carbonized by the strong acid. It is readily soluble in glacial acetic acid, and on diluting the solution with water both camphor and pyroxyline are reprecipitated. It is rapidly soluble in warm, moderately concentrated nitric acid (four volumes of fuming acid to three of water), and is also dissolved with ease by a hot concentrated solution of caustic soda. Ether dissolves out the camphor from celluloid, and wood-spirit behaves similarly. Ether-alcohol (3:1) dissolves both the nitro-cellulose and camphor, leaving the coloring and inert matters as a residue. The density of celluloid ranges from 1.310 to 1.393. When heated to 125° C., it becomes plastic and can be moulded into any desired shapes. Separate pieces can also be welded together by simple pressure when at this temperature. The celluloid is easily cemented to wood, leather, etc., by the use of collodion or a solution of shellac and camphor in alcohol.

# IV. Analytical Tests and Methods.

Pure hexanitrate of cellulose will keep indefinitely, but the presence of free acid, of lower nitrates, or of fatty and waxy matters renders it more or less unstable, and therefore unsafe. The most important determinations to make are the examination for free acid and for lower nitrates, and the valuation by means of the estimation of NO<sub>2</sub> liberated from any sample.

- 1. Examination for Free Acid.—This may be detected by treating twenty grammes' weight of the gun-cotton with fifty cubic centimetres of cold water. After twelve hours the water may be pressed out, filtered and twenty-five cubic centimetres titrated with decinormal caustic alkali. With the remainder of the liquid the nature of the acid, whether sulphuric or nitric, may be ascertained by the usual tests.
- 2. Examination for Lower Nitrates.—These may be detected it present by treating five grammes of the sample, previously dried a 100° C., with one hundred cubic centimetres of a mixture of three part of ether and one of alcohol. The mixture is shaken frequently during twelve hours, and then rapidly filtered through loosely-packed glass wool, the filtrate evaporated at a gentle heat, and the residue weighed.
- 3. EXAMINATION FOR UNALTERED CELLULOSE.—This may be estimated by treating the gun-cotton left undissolved by the ether-alcohol with acetic ether, which dissolves the hexanitrate and leaves the unchanged cotton. An alternative plan is to prepare a solution of sodium stannit by adding caustic soda to a solution of stannous chloride until the precipitate at first formed is just redissolved. This solution when boiled with gun-cotton dissolves the cellulose nitrates without affecting the unchanged cellulose. Sodium sulphide is also used for the same purpose
- 4. VALUATION BY DETERMINATION OF NO..—The nitrogen peroxid contained in gun-cotton and similar nitrated products is frequently determined by the aid of the reaction of sulphuric acid and mercur upon the nitrates as carried out in a Lunge's nitrometer. burette provided at one end with stopcock and funnel-tube and nai rowed at the other end, which is connected by a stout piece of rubbe tubing with a simple graduated burette-tube. The burette with the stor cock is filled with mercury through the rubber connection with the othe tube and the stopcock closed. .35 gramme of gun-cotton, dissolved i five cubic centimetres of concentrated sulphuric acid, are then put int the funnel-tube, and by opening the stopcock and lowering slightly th connecting burette are drawn into the stoppered tube, washed out ( the funnel with a little additional pure sulphuric acid, and the stopcoe closed. The tube is then shaken vigorously until the reaction is complet and the volume of gas no longer increases. It is then allowed to attai constant temperature and the volume read off with correction for ten perature and pressure. Allen (Commercial Organic Analysis, 2d ec vol. i, p. 328) recommends that the volume be compared with the yielded by a standard sample or a nitre solution.

### ARTIFICIAL SILK.

#### I. Raw Materials.

The manufacture of an artificial silk (with the exception of or process, not now commercially followed—that using gelatine) star with cellulose, usually in the form of the cotton fibre. Three process have been developed, until at present they have assumed what may termed an international importance and are successfully supplying

product of great value and one that has created a field for itself in numerous special utilizations. While the raw material is primarily cellulose in all cases, in two of the processes it is first changed into a chemical derivative of cellulose which is afterwards decomposed in the process of manufacture.

- 1. NITROCELLULOSE OR CHARDONNET PROCESS.—The starting-point of this process, the earliest of the commercial processes (1888) is a pure cellulose, usually cotton fibre, cleansed both mechanically and then by treatment with weak alkali solutions. This is then carded so as to open it up and nitrated, as already described in the manufacture of pyroxyline or soluble cotton. The washing of the nitrocellulose must be very thorough, so that every trace of acid is removed. When washed the wet nitrocellulose is pressed in hydraulic presses until the per cent. of water retained is reduced to thirty-six per cent., which amount remains in it until after the spinning. The solution of this is then effected in a mixture of equal parts of ninety-five per cent. alcohol and other, using one hundred litres of solvent for twenty-two kilos. of nitrocellulose, reckoned on dry weight. This solution takes place in horizontal revolving iron cylinders lined with tin and provided with mechanical agitation. From fifteen to twenty hours slow continued revolution of the cylinder is usually required and the solution, although appearing perfectly clear, is nevertheless filtered to remove any imperfectly dissolved nitrocellulose. The solution after filtration is stored in large containers to "ripen," so that it may be suited for the spinning process.
- 2. The Cuprammonium Process.—The raw material is here also a purified cellulose. Cotton is treated with an alkaline lye to bring it into a pure condition easily soluble in the solvent, which in this case is a copper-oxide-ammonia solution. Pauly, the first patentee of artificial silk of this kind, prepared his solution by precipitating cupric hydroxide from copper sulphate solution with ammonia in required amount, washing the same and then dissolving it in aqua ammonia to clear solution, of which one litre contained from ten to fifteen grammes of copper. This is then allowed to act on the moist purified cellulose in a hollander, in which the cellulose solution is rapidly effected. Even after perfect solution seems to have been effected, this must be filtered in order to obtain that uniform solution needed for the spinning opera-A later process (that of Bronnert, Fremery and Urban) prepares the cuprammonium solution by the action of strong ammonia water on metallic copper in the presence of a current of air. If the temperature is kept down to about 5° C. the ammonia in the presence of air has a rapid solvent action on the copper, and solutions containing eight and ten per cent. of copper are obtained.
- 3. The Viscose Process.—Cross, Bevan, and Beadle in 1892 discovered the method of preparing a water-soluble cellulose xanthogenate by the reaction of carbon disulphide upon alkali-treated cellulose, which compound decomposes with the liberation of carbon disulphide, leaving behind a pure cellulose in gelatinous form mixed with the alkali.

For the manufacture of filaments a short-fibre cellulose is chosen.

which is mixed with the required amount of sodium hydroxide in solution and allowed to react, producing a swollen mass of crumbling granulated texture, with the development of heat. The proportions usually taken are air-dried cellulose 25 to 33, sodium hydroxide 12.5 to 16, water 62 to 55. The carbon disulphide is made to act upon the soda-cellulose in the proportion of 1 to 10. The proper mixture being put into a wooden rotating drum which can be sealed, the reaction takes place rapidly at the ordinary temperature, a few hours sufficing for its completion. The product of the reaction being transferred to a closed vessel provided with mechanical stirring attachment, water is gradually added, when the mass dissolves to a viscid jelly which, when filtered, is ready for the spinning.

#### II. Processes of Manufacture.

SPINNING OF THE ARTIFICIAL SILK FILAMENT.—While in each case the spinning is effected by forcing a very viscid liquid through fine jets of glass or metal, the conditions are so dissimilar in the case of the three different raw materials that the process will be described as applying to each material in turn.

- 1. The Collodion or Chardonnet Process.—The collodion filament solidifies almost in the moment that it is forced out of the jets. The passing of the filament into a bath of acidified water is no longer practised, but the filament goes into the air, liberating the vapors of alcohol and ether which are carried along by a current of warm air and pass through condensation and absorption vessels, the first containing soda and the second sulphuric acid which absorbs the vapors of ether. The Chardonnet filament is, however, a nitrocellulose which when dried thoroughly is extremely inflammable, so that it is necessary to denitrate it. This is done by the action of alkaline sulphides, such as ammonium sulphide. Following this a slight bleaching is necessary, as the ammonium sulphide leaves the filament yellow. A very small amount of bleaching powder and muriatic acid suffices to bring the silk to a white color, when it is finally washed and dried.
- 2. The Cuprammonium Process.—The material which is forced from the spinning jet in this case is cellulose in ammoniacal cupric-oxide solution. So to form the filament it must be delivered into a solution which will act at once to decompose it and liberate the cellulose, which then forms a filament semisolid at first but becoming stronger as it loses the water with which it is charged. Pauly first used fifteen per cent. sulphuric acid as the ingredient of the decomposing bath. This forms cupric and ammonium sulphates, both soluble, while the cellulose filament when thoroughly washed free from acid is dried under tension and yields a product of silky lustre that requires no denitrating or bleaching to finish it.

Bronnert, Fremery, and Urban later improved this procedure by using fifty per cent. sulphuric acid in the decomposing bath, which gave

them a firmer filament, and then, after washing this, drying it in two stages, first in a current of air at the ordinary temperature and then in heated rooms at 40° C.

3. Viscose Process.—The separation of cellulose from viscose solutions takes place so readily that at first it was sought to simply spin the filament from the fine jets into a vertical shaft or air-passage through which warm air was rising, but now it is effected according to the Stearns' process by spinning the filament into a solution of ammonium chloride, which causes a complete separation of the cellulose of the filament. It is left in a cold ammonium chloride bath for several hours, brought into boiling ammonium chloride for a few minutes and then thoroughly washed.

## III. Products.

Artificial silk as a commercial product is of a uniform white color and possesses the characteristic lustre of natural silk. Chardonnet silk indeed possesses a higher lustre than the natural, although it does not have the rustle of true silk and is somewhat harder to the touch; cuprammonium silk (the German glanz-stoff), on the other hand, has more exactly the lustre as well as the rustle of natural silk; viscose silk resembles the collodion silk.

Several points of difference in physical characters between natural and artificial silk are thus given by Süvern:\*

Specific gravity.	Percentage of moisture at 99°C.	Absorption of moisture in moist room of silk dried at 110°-115°.
Natural raw silk 1.36	7.97	20.11
Chardonnet silk (1) 1.52	10.37	27.46
Chardonnet silk (2) 1.53	11.17	28.94
Lehner silk	10.71	26.45
Cuprammonium silk (Glanz-stoff) 1.50	10.04	23.08
Gelatine silk 1.37	13.02	45.56
Viscose	11.44	

That artificial silk fibres lose notably in strength on wetting is one of their distinguishing characters as compared with natural silk fibre. The average loss in strength on wetting is given as seventy per cent. for all varieties. A treatment of artificial silk with a formaldehyde bath to correct this defect has been proposed by Escalier and is known as "sthenosizing." It is claimed that fibres so treated lose very little of their strength on wetting.

From the chemical point of view the most important difference between artificial silk (the gelatine silk excepted) and natural silk is that while natural silk contains some seventeen per cent. of nitrogen, the artificial silk contains only traces of this element. They therefore behave to chemical reagents like the vegetable cellulose fibres.

<sup>\*</sup> Die Künstlicke Seide, Dr. Carl Süvern, 2te Auf., p. 220.

## IV. Analytical Tests and Methods.

There are a number of reagents that will distinguish between natural and artificial silk. Strong potassium hydroxide solution, which will dissolve natural silk, will only swell more or less the artificial silks, with the exception, of course, of gelatine silk.

Alkaline copper-glycerine solution will dissolve natural silk (both the true and the tussah silk) but does not attack the artificial silk consisting of cellulose.

Diphenylamine sulphate, however, is one of the best of the reagents for the detection of artificial silk. Its reaction is as follows:

With natural silk	.Brown coloration.
With tussah silk	.Intense brown coloration.
With Chardonnet and Lehner silk	.Intense blue.
With Pauly or Thiele cuprammonium silk	.No reaction.
With viscose silk	

It is claimed that artificial silk is more easily affected by heat than either cotton, wool, or natural silk fibre. On heating a fabric containing mixed fibres to 200° C., the artificial silk will be destroyed and the dust can be beaten or brushed out and the loss in weight give the proportion of the artificial silk originally present.

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#### STATISTICS.

#### I. C. PRODUCTION, CONSUMPTION AND EXPORTATION OF COTTON FROM THE UNITED STATES.

			Domestic con-		
~~.		Production (in bales of 500 lbs.)	sumption (bales of 500 lbs.)	Exportations (bales of 500 lbs.)	Value of
Year.	1	pates of 200 lps.)	of 500 lbs.)	(bales of 500 lbs.)	exportations.
1905		10,804,556	4,877,465	6,975,494	\$401,005,921
1906		13,595,498	4,974,199	8,825,237	481,277,797
1907	• • • • • • • • • • • • • • • • • • • •	11,375,461	4,493,028	7,779,508	437,788,202
1908		13,587,306	5,198,963	8,889,724	417,390,665
1909		10,315,382	·	5,491,842	450,447,243

1. b. COTTON CONSUMPTION BY COUNTRIES, 1905 AND 1900. (IN BALES OF 500 LBS.

Country.	1905.	1900.
United States	4,310,000	3,856,000
United Kingdom	3,620,000	3,334,000
Continent of Europe	5,148,000	4,576,000
East Indies	1,350,000	1,139,000
Japan	875,000	712,000
Canada	130,000	105,000
Mexico	70,000	18,000
Other countries	35,000	33,000
Total	15,538,000	13,773,000
	(Census Bure	an. 1905.\

II. FLAX.—According to a United States consular report from Odessa (United States Consular Reports, March, 1891, p. 365), the total area sown in Europe with flax amounted to 5,700,000 acres, of whice Russia alone had 3,700,000 acres. The total quantity of flax fibre produced in Europe is there given as follows:

Russia Austria-Hungary Germany France	104,400,000 97,200,000	Belgium	43,200,000
Ireland		1,	,350,000,000

The world's production of flax is thus stated by J. Scott Keltie (Th Statistician's Year-Book, London, 1907):

Durania	Tons.	Const Dellate and Total	Tons.
	-	Great Britain and Ireland (1908)	0.000
		Italy	
North America			-,

The importation of flax into the United States was as follows:

	1906.	1907.	1908.	1909.	1910.
Amount in tons		8,656	9,528	9,890	12,761
Value	\$2,327,300	\$2,086,205	\$2,514,680	\$2,542,256	\$3,417,321

#### III. a. The importations of other vegetable fibres have been:

	1906.	1907.	1908.	1909.	1910.
Hemp (dutiable) .	5,317	8,718	6,213	5,208	6,42
Value	\$906,808	\$1,534,371	\$1,086,805	\$799,164	\$1,039,83
Hemp (Manila)	58,738	54,513	52,233	61,622	92,50
Value	\$11,036,667	\$10,876,107	\$8,974,617	\$7,156,091	\$10,517,10
Jute (tons)	103,945	104,489	107,533	156,685	68,15
Value	\$6,449,684	\$8,950,684	\$6,504,920	\$7,216,307	\$3,728,44
Sisal grass (tons)	98,037	99,061	103,994	91,451	99,96
Value	\$15,282,308	\$14,959,415	\$14.047,369	\$10,215,887	\$11,440,52

# III. b. Production and exportation of jute from India:

	Production in 1000 cwts.	Export in 1000 cwts.
1905	29,075	12,875
1906	32,880	14,480
1907	35,064	15,970
1908		14,192
1908	***************************************	17,880
	(Statistical Abstracts for British Colonies, London,	1909.)

# IV. Paper and Pulp Statistics:

The importations of crude paper stock (rags, etc.) and of wood-pulp in recent years have been:

(	rude paper stock.		Wo	od-pulp.	
1904	. \$2,900,713	289,592,000	lbs.,	valued	at \$3,602,668
1905	. 3,796,595	335,008,000	"	"	4,500,955
1908	. 3,675,926	532,031,360	**	<b>6</b> 6	7,313,326
1909	. 3,638,034	614,244,972	"	66	8,629,263
1910	. 5,206,877	847,440,759	66	66	11,768,014
	(Commerce and	Navigation of	of U	S., 19	10.)

The production of wood-pulp, according to Census Reports, has been:

	Ground wood-pulp.	Soda-fibre.	Sulphite-fibre.	Total.
1900	586,374 tons	177,124 tons	416,037 tons	1,179,535 tons
1905	968,976 tons	196,770 tons	756,022 tons	1,921,768 tons

#### CHAPTER IX.

#### TEXTILE FIBRES OF ANIMAL ORIGIN.

As before stated, the only animal fibres that have acquired technic importance are the wool fibre and silk. These will now be considered.

#### I. Raw Materials.

A. Wool.—Wool is undoubtedly a variety of hair, found in great or less quantity on almost all mammals, on a few of which, as the domestic sheep, it forms the principal covering of the body. probable that while both hair and wool occur together in wild shee domestication has gradually caused the rank hairy fibres to disappea and the soft under-wool to develop until the fleece of wool becomes thick and complete covering. From ordinary hair the wool is disti guished by two important properties: First, while hair is almost smoot on the surface, the wool fibre is covered by minute overlapping scalarranged like roof-tiles. While these scales are so minute as not to l discernible to the eye, they can be felt if a woollen fibre is drawn betwee the fingers in the direction opposite to that in which the scales are se Secondly, while a hair is perfectly straight, the woollen fibre is fine crimped or curled, so that it becomes longer when drawn out ar shortens again when the strain is removed. The spring due to th curled structure gives woollen fabrics notable elasticity. Owing to the overlapping scale-like structure and the crimpled condition of the fibr wool has also the power of felting, or becoming matted into a compa cloth under the fulling process without the necessity of weaving. The structural characters of the wool fibre are shown in Fig. 88.

Sheep's wool varies from the long straight coarse hair of certain varieties of the English sheep (Leicester, Lincolnshire, etc.) to the comparatively short wavy fine soft wool of the Spanish and Saxon Electorsheep. According to the average length of the fibres or staples two principal classes of wool are established, the long-stapled (eighteen twenty-three centimetres) and the short-stapled wools (two and fivenths to four centimetres). The former class have hitherto bee combed and then spun into worsted yarn, while the latter have bee carded and spun, yielding woollen yarns. These processes will be referred to again later. (See p. 350.) In general the long straight wool like Lincoln and Leicester wools, possess a silky lustre, and are known as lustre wools, while the Merino, Colonial, etc., which are shorter an curly, are known as non-lustre wools.

The worth of any grade of wool is determined by noting such properties as softness, fineness, length of staple, waviness, lustre, strengthelasticity, flexibility, color and the facility with which it can be dyes

Wool is very hygroscopic. In warm dry weather it may contain eight to twelve per cent. moisture but if kept for a time in a damp atmosphere it may take up thirty to fifty per cent. This becomes an important item in the sale of wool, and hence in France and Germany the percentage of moisture contained in wool to be sold must be officially determined in "wool-conditioning" establishments. (See silk-conditioning, p. 348.) The legal amount of moisture allowed on the Continent is 18.25 per cent.

The best kind of wool is colorless, but inferior grades are often yellowish, and sometimes even brown or black in color.

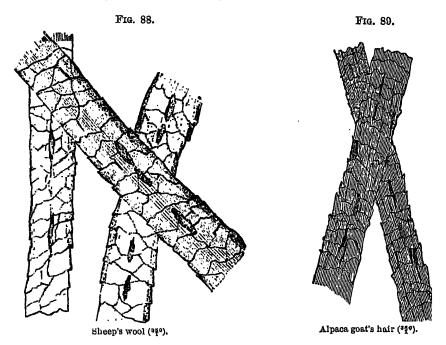
The chemical composition of the wool fibre is, as already noted (see p. 302), nitrogenous, but we must at the same time distinguish between the true fibre and the encrusting matters. These latter, independent of mechanically adhering impurities or "dirt," are of twofold character, the "wool-fat" (soluble in ether) and the "wool-perspiration" (soluble in water). These two are frequently included together under the name of the "yolk" or "suint" of the wool. The true wool fibre, when cleansed from these, has approximately the following composition: Carbon, 49.25 per cent.; hydrogen, 7.57 per cent.; oxygen, 23.66 per cent.; nitrogen, 15.86 per cent.; sulphur, 3.66 per cent. The presence of sulphur is very distinctive of wool and serves to distinguish it from silk, the other nitrogenous fibre. It can be removed in large part, but not without weakening the fibre and destroying its lustre, etc.

Wool-fat is a mixture of a solid alcoholic body, cholesterine, together with isocholesterine and the compounds of these bodies with several of the fatty acids. These free higher alcohols are soluble in boiling ethyl alcohol, while the compounds they form with the fatty acids are insoluble in alcohol but soluble in ether.

Wool-perspiration has been shown to consist essentially of the potassium salts of oleic and stearic acids, possibly other fixed fatty acids, also potassium salts of volatile acids, like acetic and valerianic acid, and small quantities of chlorides, phosphates, and sulphates. The washwater of raw or greasy wool, it will be seen, therefore, would contain large amounts of potash salts, and when evaporated and ignited would yield an abundant product of potassium carbonate. This utilization of the wool wash-water as carried out at present in France and Belgium yields over one million kilos. of potassium carbonate. Another utilization of this yolk of wool is to submit it to dry distillation, when it yields a residue which is an extremely intimate mixture of carbonate of potash and nitrogenous carbon, of great value for the manufacture of yellow prussiate of potash.

Wool is decomposed by heat at 130° C., ammoniacal vapors are given off, and at 140° to 150° C. sulphur compounds are also present in the vapors. When ignited by a flame, wool emits the disagreeable odor of burnt feathers and leaves a porous caked residue. Ammoniacal solution of cupric hydroxide has no action upon wool in the cold, but dissolves it when hot. Dilute solutions of hydrochloric and sulphuric acids have little influence whether hot or cold. This fact is availed of in separating

cotton from wool in the process of "carbonizing" mixed cotton ar woollen goods. The dilute sulphuric acid used attacks and disintegrat the cotton. They are then dried in closed chambers at 110° C., aft which the disorganized cotton can be beaten out, while the wool remain but slightly altered. Nitric acid does not attack the wool seriously, be gives it a yellow color, hence sometimes used as a "stripping" agent for dyed woollen goods in case of re-dyeing. Sulphurous acid is the mosatisfactory bleaching agent for woollens, as it removes the nature yellow tint of the ordinary wool. Caustic alkalies act rapidly and i juriously upon wool. Alkaline carbonates and soap have little or injurious action if not too concentrated and if the temperature is n above 50° C. Chlorine and hypochlorites act injuriously upon wool at cannot be used for bleaching. A very slight action of chlorine, on the other hand, causes wool to assume a yellowish tint and gives it increased affinity for many coloring matters.



Closely related to sheep's wool are a few varieties of animal hai which are also utilized in some degree as textile fibres in similar class of goods.

Mohair is the product of the Angora goat of Asia Minor and Ca<sub>l</sub> Colony, South Africa. It is a long silky hair, which is very soft ar lustrous.

Cashmere consists of the soft under-wool which grows in winter the Cashmere goat. It furnishes the material for the costly Cashme shawls of native manufacture, but is not exported at all as fibre.

Alpaca, Vicuna, Llama, and Guanaco are the names of four closel

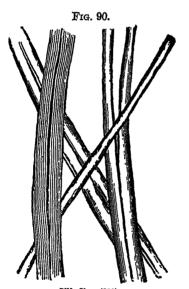
related species of South American goats found on the western slopes of the Andes, which yield valuable hair-like fibres. Of these, the alpaca is exported in largest amount to Europe and the United States. It is a long silky fibre somewhat intermediate between true wool and hair and possessing a strong lustre. It is both white and of various colors. It is shown in Fig. 89.

Camel's Hair is somewhat used in Africa, Asia Minor, and the Caucasus, and latterly in Europe, for the manufacture of woven goods, which are made from the unbleached hair.

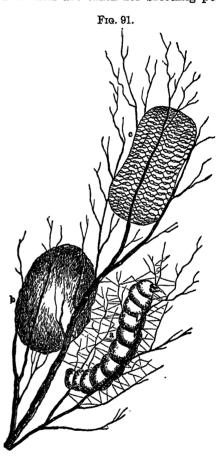
B. Silk.—The silk fibre is, morphologically, the simplest and at the same time, because of its properties, the most perfect of the textile fibres. It differs from all the other fibres in that it is found in nature as a continuous fine thread, so that the process of spinning is superfluous in its case. In place of this we have the reeling process, whereby several of the natural threads are united into one thicker and stronger thread.

Silk is the product of the silk-worm (Bombyx mori) and is simply the fibre which the worm spins around itself for protection when entering the pupa or chrysalis state. From the eggs laid by the animal in the moth or butterfly state develops the caterpillar or silk-worm. The eggs are yellowish in color at first, changing to gray when dry. They are very light in weight, some thirteen hundred and fifty together weighing one gramme. For the development of the caterpillar from them a certain amount of warmth and moisture is necessary, the temperature being raised in the incubation chamber during ten or twelve days from 18° to 25° C. The young worms are at once removed to larger chambers. where are lath frame-works strung across with threads and sheets of paper. The animals are placed upon these, and fed regularly during thirty to thirty-three days, till indeed they begin to spin. They are here fed upon mulberry leaves (Morus alba), and during this period increase enormously in size, becoming at length about eight to ten centimetres long and about five grammes in weight. To allow of this increase in size it casts its skin some four times during this period (at intervals of from four to six days). When about the thirtieth day of its growth has been reached it ceases to take food and shows a decided restlessness. It is then placed on birch-twigs, and soon begins to spin. This spinning of the cocoon, or oval-shaped house in which the worm is to undergo the chrysalis state before emerging as the butterfly, involves the secretion of the fibre so much prized as silk. The silk substance is secreted by two glands, one on either side of the body of the caterpillar. The substance from these two glands unites in a capillary canal situated in the head of the animal, whence issues the silk as a double fibre only rarely separated, cemented throughout by the sericin, or silk-glue. The microscopical appearance of the silk fibre is shown in Fig. 90. This fibre which goes to form the cocoon varies in length from three hundred and fifty to twelve hundred and fifty metres, and has a diameter which averages about .018 millimetre. The interlacing layers of the silk cocoon are at first loose, but become finer and denser towards the interior, while the innermost layer which immediately surrounds the animal forms a th parchment-like skin. The several stages of cocoon-spinning are show in Fig. 91. The cocoons of the female are pure oval in shape, while the of the male are distinctly contracted in the centre. They are white yellowish, and usually about three centimetres long and one and or half to two centimetres thick. Some seven or eight days are allowed f the completion of the cocoon-spinning, and they are then gathered. sufficient number of both males and females are taken for breeding pu

poses, and the rest put aside to be reeled for silk. Those chosen for breeding are kept for some twenty days at a temperature of from 19° to 20° C., when the silk-moth which has formed in the interior from the pupa emits a peculiar saliva, which softens the sericin, or silk-glue, at







one end of the cocoon and enables the animal to push its way out to da light. The females within forty hours after their appearance lay the eggs, some four hundred in number, and shortly after die. The eg are slowly dried, and stored in glass bottles in a dry dark place till to following spring. The cocoons put aside for the reeling of silk mube taken in hand promptly and the chrysalis contained in them kille in order to prevent the development of the silk-moth and the injury the cocoon by its pushing its way out. This is done either by heating them for several hours in an oven at 60° to 70° C., or more quickly leading to the silk-moth and the injury the cocoon by its pushing its way out.

steam heat. One hundred grammes of eggs produce under favorable conditions from ninety thousand to one hundred and seventeen thousand cocoons, weighing one hundred and fifty to two hundred kilos., and these yield twelve to sixteen kilos. of reeled silk.

The silk fibre consists to the extent of rather more than half its weight of  $fibr\ddot{o}in$ ,  $C_{15}H_{23}N_5O_6$ , a nitrogenous principle. Covering this is the silk-glue, or sericin,  $C_{15}H_{25}N_5O_8$ . Whether this latter exists in the glands of the silk-worm along with the fibr\ddot{o}in, as maintained by Duseigneur-Kleber, or is produced exclusively by atmospheric change from the fibr\ddot{o}in as asserted by Bolley, is still in debate. This sericin, however, is easily dissolved off from the fibr\ddot{o}in by warm soap-water and other alkaline liquids. This "boiled-off" liquid plays an important part in silk-dyeing operations. (See p. 544.) The most important physical properties of the silk fibre are its lustre, strength, and avidity for moisture. The regulation of the amount of moisture contained in raw silk as offered for sale, or "silk-conditioning," will be spoken of under the process of treatment. (See p. 348.)

Besides the true silk, the product of Bombyx mori, we have several so-called "wild silks," the most important of which is the Tussur silk, the product of the larva of the moth Antherœa mylitta, found in India. The cocoons are much larger than those of the true silk-worm, eggshaped, and of a silvery drab color. They are also attached to the twigs of the food trees by a thread-like prolongation of the cocoon. The cocoon is very firm and hard, and the silk is of a drab color. It is used for the buff-colored Indian silks, and latterly largely in the manufacture of silk plush. Other wild silks are the Eria silk of India, the Muga silk of Assam, the Atlas or Fagara silk of China, and the Yama-mai silk of Japan.

## II. Processes of Manufacture.

It will be beyond the province of this work to take up the manufacture of woollen and silk goods from the mechanical side. Hence we shall only notice the preliminary processes of chemical treatment which the fibres undergo to prepare them for manufacture into goods, and then take up the several classes of manufactured textiles again in speaking of bleaching and dyeing of goods.

A. Wool.—1. Wool-scouring.—The condition of the raw wool when first obtained from the back of the sheep has already been referred to. The fibre is covered with both natural and artificial impurities (yolk, dirt, etc.) to such an extent that mordanting and dyeing would be almost impossible. These are therefore to be removed by the process of scouring. It will be remembered, too, that the yolk was stated to be made up of the wool-fat (soluble in alcohol) and the wool-perspiration (soluble in water). Both of these have to be removed in the completed scouring operation. The full operation then must include three stages,—viz., steeping, or washing with water (désuintage); cleansing or scouring proper with weak alkaline solutions (dégraissage); rinsing or final washing with water (rinçage). The first operation may be omitted if the

wool has been washed by the wool-grower. This is true, for instance with Australian wools, while, on the other hand, most South American wools come into commerce unwashed and very rich in yolk. The wash ing of these wools is largely carried on in France and Belgium, and as has been stated (see p. 342), is made to yield large amounts of potas sium carbonate by evaporating and igniting the wash-waters. The woo is systematically washed in tepid water (about 45° C.) in a series o tanks arranged so that the water passes from one to the other unticompletely saturated, when it is evaporated. According to M. Char delon, one thousand kilos. of raw wool may furnish three hundred an thirteen litres of yolk solution of specific gravity 1.25 (50° Tw.), havin a value of fifteen shillings and sixpence, while the cost of extractio does not exceed two shillings and sixpence.

The scouring and washing processes for loose wool are usually carrie out in the well-known rake scouring-machines, consisting of a larg cast-iron trough provided with an ingenious system of forks or rake whereby the wool is gradually passed forward by the to-and-fro diggin motion of the rakes. Two or three such scouring-machines are place in series, so that the first may take the bulk of the impurities, the secon complete the scouring, and the third effect a thorough washing in stream of fresh water. The scouring liquid which has been longest i use is stale urine (lant), which is effective because of the ammonium carbonate it contains. It is now largely supplanted by ammonia, sodiu: carbonate, soaps, etc. The most injurious effects arise from the use ( water containing lime or magnesia, because of the formation of th insoluble lime or magnesia compounds upon the fibre. In recent year volatile solvents, like petroleum-naphtha, carbon disulphide, and carbo tetrachloride, have also been introduced for scouring purposes, althoug not generally adopted on account of the expense and risk attending the use. They must be followed at all events by a washing with water, a while they dissolve fatty matters, they do not take up the cleates, etc of the wool-perspiration.

The only treatment of this kind, known technically as a degreasin process, is that with petroleum-naphtha. This has been found praticable and remunerative. The wool, freed from its grease and wa like constituents by the naphtha and its potash salts, by a washing wiwater only is left in an excellent condition for the mechanical treatmer such as carding and combing.

Woollen yarns and woollen cloth are also scoured to free them fro the oil which has either purposely or by accident been put upon the in the spinning and weaving operations. The scouring of "union goods—that is, materials with cotton warp and woollen weft—is a mo difficult operation on account of the differences in elasticity, hygr scopic character, etc., of the cotton and the wool fibre. It includes t operations of crabbing, steaming, and scouring.

2. Bleaching Wool.—Wool is generally bleached either as yarn cloth. The bleaching agent in general use is sulphur dioxide. It most course be applied either as gas or as sulphurous acid solution, t

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former method being generally followed, and the yarn or cloth suspended on poles in closed chambers, called sulphur-stoves, which can be charged with the gas. In liquid bleaching with sulphurous acid, a solution of sodium bisulphite is generally used, which is either mixed with an equivalent amount of hydrochloric acid or, what is better, the goods are passed through one solution after the other in separate baths. The bleaching of sulphur dioxide differs essentially from that effected by chlorine and hypochlorites in that it is not due to oxidation, but to reduction or possibly to the formation of colorless compounds with the natural yellow color of the wool. At all events, it is not permanent in character, and the yellow color gradually returns on exposure to atmospheric influences and repeated washings in alkaline solutions.

The best liquid bleaching agent is hydrogen dioxide. The woollen material is steeped for several hours in a dilute and slightly alkaline solution of the commercial  $H_2O_2$  and then well washed, first with water acidified with sulphuric acid and afterwards with pure water.

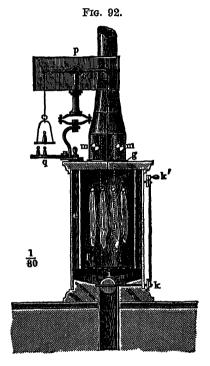
- B. Silk.—1. Reeling of Silk.—The unwinding of the long silk fibre from the cocoon and bringing it into condition for weaving is to be accomplished in the reeling process. The cocoons are thrown into a basin of warm water to soften the silk-glue and allow of the fibres being separated. From four to eighteen fibres, according to the quality, are taken, and two threads formed by passing the fibres together through two perforated agate guides. After being crossed or twisted together at a given point they are again separated and passed through a second pair of guides, thence through the distributing guides on to the reel. The temporary twisting or crossing causes the agglutination of the individual fibres of each thread. In order to form long threads a frequent adding on the fibre of a new cocoon is necessary. Care must be taken, also, that the thread remain as nearly as possible of uniform thickness, so that as the inner fine fibres of several cocoons come through the guides another cocoon is added to the number used for the thread. One cocoon gives .16 to .20 or at most .25 gramme of raw silk. The loss through removal of the external floss varies from eighteen to thirty per cent., according to the cocoons and the care bestowed by the worker. Before this raw silk can be used for weaving two of the threads are "thrown" together and slightly twisted.
- 2. Silk-conditioning.—Raw silk kept in a humid atmosphere is capable of absorbing thirty per cent. of its weight of moisture without this being at all perceptible. It therefore becomes a matter of great importance for the buyer to know what weight of normal silk there is in any given lot. To ascertain this with accuracy, there have been established in a number of the European centres of silk industry conditioning establishments. The operation is carried out by means of the apparatus shown in Fig. 92, where a number of hanks of silk are shown in the drying chamber. A test hank of silk is taken from the bale, and having been suspended from the one arm of an accurate balance its initial weight is gotten. It is then dried in a current of air at 110° C. until constant weight is again obtained. The arrangement of the drying

chamber is shown in the illustration. To the final weight obtained for the dry silk eleven per cent. is added, and the result taken as a normal silk weight. The average loss of weight in this conditioning process is about twelve per cent.

3. Silk-scouring.—By the scouring of silk the silk-glue is removed to a greater or less extent and the fibre is rendered lustrous and soft and able to take the dye-color. According to the amount of silk-glue removed in this operation the product is called boiled-off silk, souple silk, or écru. In the first case, the loss of silk-glue amounts to twenty-five to thirty

per cent. of the weight of the raw silk; in the second, to eight to twelve per cent.; and in the third to three to four per cent. of the original weight of the silk. In preparing the first variety two operations are necessary, stripping or ungumming (dégommage), and boiling off.

The hanks of raw silk are suspended by wooden rods in a rectangular trough lined with copper and worked by hand in a thirty to thirtyfive per cent. soap solution heated to 90° to 95° C. When the water is very hard it must be corrected or softened previously. Frequently two soapbaths are used one after the other as the first one becomes charged with the The silk at first swells up and becomes glutinous, but as the glue dissolves off it becomes soft and silky. The waste soapy and glutinous liquid obtained is called "boiledoff" liquor, and is a useful addition to the dye-bath in dyeing with coal-



tar colors. (See p. 544.) For the purpose of removing the last portions of the silk-glue, it is now washed in water at 60° C., to which some soap and carbonate of soda have been added, then put in coarse hempen bags called "pockets" and boiled for half an hour to three hours, according to quality, in open copper vessels with a solution of ten to fifteen per cent. of soap. It is then rinsed with a weak tepid solution of sodium carbonate, and finally washed in cold water. Silk intended to remain white or to be dyed pale colors is then at once bleached while moist with gaseous sulphur dioxide for some six hours. The bleaching operation may be repeated from two to three times, according to the quality of the silk.

Souple silk is that which has been prepared for dyeing with a loss of not more than eight per cent. of its weight. It is, however, not so strong as boiled-off silk, and is used only for tram. Its preparation

always includes two operations, and if the silk is to be dyed light colors, two additional operations have to be carried out. The raw silk is first "softened," and the small quantity of fatty matter present removed (dégraissage) by working it from one to two hours in a ten per cent. soap solution at 25° to 35° C. It is then "bleached" by immersion for ten to fifteen minutes in a dilute solution of aqua regia (five parts hydrochloric acid to one part nitric), or as a substitute for this nitrated sulphuric acid (nitrosyl-sulphate). This is followed by "stoving," or treatment with sulphur dioxide, and then, without removing the sulphurous acid, by the treatment of soupling (assouplissage) proper. This consists in working the silk for about an hour and a half at 90° to 100° C. in water containing three to four grammes cream of tartar to the litre. This treatment makes the silk softer and causes it to swell up and become more absorbent. It is then finally washed in tepid water.

Ecru silk is raw silk which has been washed with hot water, with or without soap, bleached with sulphur, and again washed. It is only used for a base for other silk fabrics like velvet or dyed in blacks.

Artificial silk has already been described in detail under the vegetable fibres and the products therefrom (see p. 333.)

## III. Products.

A. WOOL.—We have already alluded to the distinction between worsted and woollen yarns. Formerly all long-stapled wools were combed,—that is, the fibres were brought as nearly as possible parallel to one another and were then spun into what was known as worsted yarn, used in hoisery and in the manufacture of fabrics which did not undergo fulling. All short-stapled wools, on the other hand, were carded and spun much as cotton is spun, and the yarns so obtained were the only ones capable of being used in making milled or fulled cloths, in which the felting property of wool is availed of to thicken the cloth after weaving and in which by teasels the nap of the cloth is raised so as to present a uniform surface. All kinds of wool, therefore, were formerly divided into combing and carding or clothing wools. Machines have been invented latterly, however, capable of combing wools having as short a staple as one inch, and, on the other hand, wools with a staple as much as five inches long may be used in making milled cloth. So the distinction between the several wools is no longer as absolute as it once was.

Among the chief kinds of worsted fabrics are serges and merinos and mixed goods of wool and mohair, alpaca, and camel's hair. Hosiery and carpets also belong here, although the best of these latter are made on a ground of strong linen or hemp. The principal varieties of woollen cloth are broadcloths, the finest variety of woollen cloth, cashmeres, a fine thin twilled fabric, tweeds, fabrics of looser texture than broadcloth and less highly milled, doeskin, a strong twilled cloth, blankets, flannels, etc.

Shoddy is a material made from fragments of cast-off woollen clothing torn into fibres and re-spun into yarn. It is looser in texture than

mungo, which is made from remains of finer fragments, such as old dress-coats, tailor's clippings, etc.

A third grade of recovered wool, sometimes called extract wool, i obtained from union goods (mixed woollen and cotton goods) by th process of carbonizing the vegetable fibre and then beating it out. Th carbonizing is done with dilute sulphuric acid, with aluminum chloride or with gaseous hydrochloric acid. The last process is said to give th best results.

B. Silk.—The raw-silk threads obtained in the reeling process ar not sufficiently strong for use in the loom, so several must be united. This may be done in different ways. By the union of two or more single threads, separately twisted in the same direction, which are then double and retwisted in the opposite direction, is obtained organzine. The begrades of silk are also taken for the organzine, which is to form the war in silk-weaving. The product of the union of two or more simple untwisted threads which are then doubled and singly twisted is tram, which forms the weft in weaving.

Waste silk is that which proceeds from perforated and double cocoon and such as are soiled in steaming or in any other way. This wast silk is washed, boiled with soap, and dried. When carded and spun lik cotton it yields the so-called flurt-silk.

Satins are tissues so woven that almost the only threads appearin on the right side of the tissue are weft threads, which present a uniforglossy surface.

Velvets are tissues in which the outer surface presents to view short soft pile, made by passing the warp threads over fine wires, whice are afterwards drawn out. The loops then remaining are either left they are, in which case the tissue is called pile-velvet, or cut to for cut-velvet. This fabric is now largely imitated in cotton and mixet tissues.

# IV. Analytical Tests and Methods.

GENERAL DISTINCTIONS BETWEEN VEGETABLE AND ANIMAL FIBRES.-A general scheme for distinguishing between the several classes of fibr has been proposed by R. Schlesinger in his "Leitfaden für die mikr skopische und mikrochemische Analyse der technisch verwendete Rohstoffe der Textil-Industrie." It is in outline as follows:

TREAT WITH CAUSTIC SODA.				
The fibre does not dissolve in ten per cent. caustic soda solution, and in burning, which takes place readily, does not develop any burnt horn odor.	The fibre dissolves in concentrated caustic soda, and when treated with ammoniacal cupric oxide shows scales upon its surface.	The fibre does not dissolve it cold ten per cent. causti soda, but dissolves per fectly in concentrated su phuric acid; shows neithe scales nor medullary sul stance.		
Vegetable fibres.	Animal hairs or wool.	Silks.		

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The vegetable fibres are then to be studied by the aid of the iodine and dilute s phuric acid reaction, and the several groups already noted in the classification on p. 3 are established.

The animal hairs are to be distinguished best by the microscopical characters as measurements.

The several varieties of silk are also to be distinguished by a comparison of the dian ters of the fibre as measured under the microscope.

A scheme for distinguishing between the more important textile fibre based upon their behavior to the two dyes malachite-green and Cong red, and after examination under the microscope, has been proposed the Behrens ("Microchemische Analyse," 2te Heft, p. 51). The groupir thus established is as follows:

Group A. Dyed fast to washing by malachite-green.

Here belong, of the textile fibres, silk, wool, and jute.

Aa. Not capable of supplementary dyeing by aromatic amines: silk as wool.

Ab. Capable of supplementary dyeing by aromatic amines: jute.

Group B. Dyed partially fast only by malachite-green.

Hemp and manila.

Ba. Strongly polarizing: hemp.

Bb. Weak polarizing: manila.

Group C. Fugitive dyeing with malachite-green; complete supplementary dy ing with benzidine dyes.

Here belong cotton and flax.

Ca. Weak polarizing: cotton.

Cb. Strongly polarizing: flax.

Several of the simpler differences between the vegetable and the animal fibres as groups have already been alluded to in classifying the fibres. (See p. 302.) Other special tests are as follows:

- 1. Millon's reagent (mercurous and mercuric nitrate) colors the animal fibres red, but not the vegetable fibres.
- 2. Liebermann gives the following test: Prepare a fuchsine solution, add potash solution drop by drop until it is decolorized, filter, an dip in the sample of goods. Wool or silk fibres are colored red, cotto remains colorless.
- 3. Ammoniacal cupric oxide solution dissolves cotton as well as sill While cotton, however, is precipitated by certain salts as well as b sugar and gum, silk is only precipitated by acids.
- 4. As wool always contains sulphur, a sodium plumbate solutio (made by boiling red lead with caustic soda solution and filtering) at once blackened on contact with wool. This test may be interfere with in the presence of sulphur-treated silk.
- 5. Wool and silk may be distinguished by the use of hot hydrochloric acid. Silk dissolves easily in this, while wool merely swells u but does not dissolve.
- 6. According to Höhnel, wild silks behave differently from true silk with chromic acid. If a cold saturated solution of chromic acid b diluted with an equal bulk of water and then boiled for one minute wit the sample of silk, the true silk dissolves up, while the wild silk remain unattacked even after two or three minutes' boiling. Wool behave like true silk in this.

A. Remont gives a process for determining wool, silk, and cotton when mixed in the same fabric. Four pieces of about two grammes weight each are taken; three of these are boiled for a quarter of an hour in two hundred cubic centimetres of three per cent. hydrochloric acid which is renewed if the liquid becomes strongly colored, and the samples are then well washed. The dressing is thus removed and the coloring matter in the case of the cotton, but only slightly in the case of woo and silk; the weighting of the silk with iron salts is also completely removed by the hydrochloric acid if the weighting does not exceed twenty-five per cent. of the weight of the silk, leaving the fibres chest nut-brown in color. Two of the samples thus treated are dipped for one to two minutes into a boiling solution of basic chloride of zinc o specific gravity 1.69; then thrown into water and washed first witl acidified water and then with pure water. This removes the silk. Th basic chloride of zinc solution is prepared by heating one thousand part of zinc chloride, forty parts of zinc oxide, and eight hundred and fift parts of water.

One of the two samples freed from silk is then boiled gently for quarter of an hour with sixty to eighty cubic centimetres of causti soda solution of specific gravity 1.02. This is best done with inverte condenser, so that an injurious concentration of the soda solution i avoided. Wash gently without too much rubbing and the wool i removed. All four samples are now washed for a quarter of an hou with distilled water, pressed out, dried in the air, and weighed. Th first will weigh as before, two grammes or nearly, a slight difference c a few milligrammes being neglected; the difference in weight betwee the first and second samples gives the dressing; that between the secon and third gives the silk; that between the third and fourth the wo present, and the weight of the fourth sample the vegetable fibre presen This is slightly attacked by the soda solution, and in the case of cotto it is usual to reckon five per cent. as the loss from this cause.

# V. Bibliography and Statistics.

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#### STATISTICS.

Wool.—The following figures show the production, importation, and home consumption of wool for the United States in recent years:

	Production.	Importation.	Home consumption.
Year.	Pounds.	Pounds.	Pounds.
1905	 295,488,428	249,135,746	542,062,536
1906	 298,915,130	201,688,668	494,960,990
1907	 298,294,750	203,847,545	498,695,547
1908	 311,138,321	125,980,524	431,252,030
1909	 328,110,749	266,409,304	590,996,078
	(01-	Alakian Alakian ing St	( 000 T

(Statistical Abstract of U.S., 1909.)

The importations of wool during the last few years are thus classified:

	1908	1909	1910
Class I.—Clothing wool (lbs.) 4	15,798,303	142,580,993	111,592,978
Valued at\$1		\$29,455,598	\$27,231,052
Class II.—Combing wool (lbs.)		21,952,259	31,614,235
Valued at		\$4,591,559	\$7,931,145
Class III.—Carpet wool (lbs.)	66,849,681	101,876,052	120,721,019
Valued at	\$9,762,122	\$11,124,837	\$16,058,647

The world's production of raw wool in 1903 was estimated to be 2666 million pounds. The chief producing country, Australia, exported as follows:

	Raw wool.		Scoured	Scoured wool.	
			Amount	Value in	
			in	1000 pds.	
		sterling	1000 lbs.	sterling	
	339,395	13,147	55,911	3,975	
	380,420	15,574	56,775	4,247	
	415,353	17,547	64,889	5,099	
		22,928	72,318	5,964	
•••••	471,846	18,028	70,915	4,886	
		Rav Amount 1000 lbs. 339,395 380,420 415,353 512,757 471,846	Amount Value in 1000 pds. 1000 lbs. sterling 1001 lbs. sterling 1339,395 13,147 15,574 15,253 17,547 1512,757 22,928	Amount Value in 1000 pds. 1000 lbs.	

(Statistical Abstract, 1909.)

After the British Colonies of Australia, New Zealand, and Cape of Good Hope, the largest wool producing country is the Argentine Republic and La Plata. The exports in bales of one hundred and twenty-five kilos. were as follows:

1900		468,000	bales.
	***************************************		
	************************************	±00,021	Daies.
1906	***************************************	419,386	bales.
1907	***************************************	384 071	holon
	***************************************	00 <del>1</del> ,011	pares.
1908	***************************************	382,000	bales.

Silk.—The production of raw silk throughout the world at five-ye intervals, as given in the Census Report of 1905, was:

	1885.	1890.	1895.	1900.	1905.
Italy (kilos)	2,810,000	3,033,000	4,661,900	4,528,500	4,900,0
France (kilos)	483,000	618,000	896,000	500,000	625,0
Austria (kilos)	142,000	267,000	266,000	276,000	315,0
Spain (kilos)	85,000	65,000	90,000	78,000	77,0
The Levant (kilos)	730,000	707,000	1,244,000	1,760,000	2,186,0
Japan, exports (kilos) .	1,346,000	2,130,000	3,076,000	3,371,000	5,679,5
China, Shanghai (kilos).	2,695,000	2,914,000	3,358,000	4,756,000	2,950,0
China, Canton (kilos) .	774,000	1,529,000	1,394,000	2,253,000	2,137,7
India, Calcutta (kilos) .	861,000	210,000	199,000	350,000	180,0
Total	9,926,000	11.473.000	15.184.900	17,932,000	19,050,3

The same report thus gives the raw silk consumption of the wor by countries, taking an average of the years 1902, 1903, and 1904:

Country. United States France Germany Switzerland Russia and Caucasus Italy Austria-Hungary England India	4,327,000 2,846,000 1,595,000 1,271,000 966,000 776,000 709,000 350,000	Pounds. 13,512,240 9,541,035 6,275,430 3,516,975 2,802,555 2,130,030 1,711,080 1,563,345 771,750	Per cent. of total. 31.0 21.9 14.4 8.1 6.4 4.9 3.0 3.6 1.8
Egypt	200.000	441,000	1.8
Spain	183,000	403,515	0.9
Syria	110,000 70,000	242,500 154,350	0.6 0.4
Algeria and Tunis	65,000	143,325	0.3
Other countries	152,000	335,160	0.8
	19,748,000	43,544,340	100.0

No data exist to show the consumption in China and Japan and the are not included.

The importations of raw silk into the United States for the last fer years have been as follows:

1905		22,357,307	pounds,	valued	at \$61,040,053
1907		18,743,904	- "	**	71,411,899
1908		16,662,132	"	66	64,546,903
1909		25,187,957	"	**	79,903,586
1910		23,457,223	"	cc	67,129,603
	(Co	mmerce an	d Naviga	ition of	U. S., 1910.)

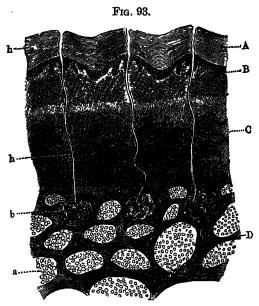
# CHAPTER X.

### ANIMAL TISSUES AND THEIR PRODUCTS.

# A. LEATHER INDUSTRY.

### I. Raw Materials.

1. Animal Hides and Skins.—The moist animal skin undergoes decomposition very rapidly; if dried it becomes stiff and horny, or if boiled with water is changed into soluble glue. The object of tanning is to bring the animal skin into such a condition that decomposition is arrested, and after drying it no longer forms a stiff horny mass, but an opaque tissue insoluble in water, distinctly fibrous and pliable. The product known as leather has properties which at once distinguish it from the untanned hide, such as greater or less impermeability to water and toughness and strength. Nevertheless, the best authorities on the



subject believe that in the main tanning is a physical rather than a chemical process, and that the function of the tanning material is chiefly to penetrate the pores of the skin and envelop the individual fibres so that in drying they are prevented from adhering and so stiffening the whole mass. The power of the skins to fix tanning materials upon the surface of its fibres varies considerably according to the nature of the material used, and in many grades of leather is undoubtedly supplemented chemical combination of the coriin of the skin with the tannin.

To understand the nature of the change wrought by tanning in the animal hide, it is necessary first to refer briefly to its anatomical structure. Fig. 93 shows a section of ox-hide cut parallel with the hair, magnified about fifty diameters. It consists essentially of three layers: the *epidermis*, which is itself made up of two layers, the outer horny layer or cuticle A, a dead layer which is continually wearing off and being renewed, and the inner mucous layer

B, the rete Malpighii, a watery cellular layer, which rests upon the tr skin and is continually renewing the outer layer; the derma or corium, t true skin, C, which alone is the leather-tissue; and the fatty und tissue, shown in the illustration at D, in which the perspiratory as sebaceous glands are embedded. Both the epidermis and the und tissue are removed in the preparatory processes of tanning, so that t corium alone remains to combine with the tanning materials to for leather. The hair of the animal is enclosed in hair-sheaths, which pa down through the epidermis and rest upon the corium, from which life the hair-glands draw their nourishment. The corium, or tr leather-forming layer, is composed of bundles of interlacing fibration between which is found an albuminoid substance, coriin, which as t skin dries cements the fibres together and stiffens the hide. This is i soluble in water but soluble in lime-water, and hence removed in lar part by the process of liming to which the hides are submitted.

The animal skins which are utilized in the manufacture of leath are, first, those of the ox, cow, buffalo, horse, etc. These are known hides, or if from younger animals of the same kind as kips. Secon those of the calf, sheep, goat, deer, etc. These are known as skins. For special purposes the skins of crocodiles, alligators, porpoises, and see are also made into leather.

The hides may come to the tannery according to the source when obtained either as fresh or green hides,—that is, direct from the slaughter-houses,—as wet salted, as dry salted, and as dried hides. I addition to the domestic production, great numbers of hides are in ported into the United States from the Argentine Republic and the River Plate in South America. England imports from India, the Cap of Good Hope, and Australia as well as from South America. Gos skins for the morocco trade are brought mainly from India and the Eas

2. Tannin-containing Materials.—The conversion of the hides in leather is usually accomplished by the action of an extract or infusic of tannin or tannic acid. This powerful astringent acid is very wide distributed in nature, being found in barks, roots, leaves, seed-pod flowers, and fruits, and in excrescences on trees. More accurately spea ing, we find a number of varieties of tannic acid in these different veg table sources, of which some are more valuable for tanning than other As a class they are readily soluble in water, amorphous, of slight ac reaction, and astringent taste. They yield with iron salts bluish-blac or greenish precipitates, throw gelatine and albumen out of solutio and change hides into leather. In tanning it is not necessary to extra the acid in a pure state, but infusions are made from the powdered barl as needed, or concentrated extracts prepared for this purpose are use We will note briefly the more important tannin-containing materia used at the present time in leather manufactures.

Oak-bark.—The common English oak (Quercus Robur), which is cludes the two varieties Q. pedunculata and Q. sessiliflora, is one of the most important materials. It contains from twelve to fifteen percent. of tannic acid and produces an excellent quality of leather. Other varieties in use are Quercus coccifera (or kermes-oak), of which the

bark, known as coppice-oak, is yellowish-brown in hue and very rich in tannin; Quercus suber (or cork-oak) and Quercus Ilex (or evergreenoak), both of which are grown in Algiers, Italy, Spain, and the South of France. In the United States the most important varieties of oak are Quercus prinus or castanea (chestnut-oak); Quercus rubra (common red-oak); Quercus alba (or white-oak). The tannin of the several varieties of oak is known as quercitannic acid. According to the researches of Etti,\* the main constituents of the oak-bark are quercitannic acid, with the formula  $C_{17}H_{10}O_0$ ; its first anhydride, phlobaphene,  $C_{34}H_{30}O_{17}$ ; its second anhydride,  $C_{34}H_{28}O_{16}$ ; its third anhydride, Oser's oak-red,  $C_{34}H_{20}O_{15}$ ; and its fourth anhydride, Löwe's oak-red,  $C_{34}H_{24}O_{14}$ . Of these, the quercitannic acid and the phlobaphene are specially concerned in the tanning process.

Hemlock-bark.—The bark of the hemlock (Abies Canadensis) of Canada and the United States contains nearly fourteen per cent. of tannin. This is extensively used, either jointly with oak-bark (union tanned leather) or as a substitute for it, in the manufacture of sole-leather. It is said to produce a harder leather than oak-bark, but less pliable and more pervious to water. A solid extract from the hemlock-bark containing from twenty-five to thirty-five per cent. of a deep red tannin is prepared in large quantities for export. The production of this solid extract is said to be at present considerably over ten thousand tons per annum. Liquid extracts with fifty per cent. of solid matter are also largely sold.

Pine-bark is much used in Austria, Bavaria, and Southern Germany. It contains from seven to ten per cent. of tannin and considerable resinous extractive matter. It does not yield so good a leather as oak-bark.

Closely related and somewhat used are the barks of the White Spruce, the Larch, and the Fir.

Willow-bark.—Several species of the willow, notably Salix arenaria and S. capræa, are used in Russia and Denmark for the tanning of lighter skins, for the manufacture of glove leather and the so-called Russia leather. It is stated that the yearly consumption of willow-bark in Russia at present is some six and a half million kilos. against two and a half million kilos. of all other tanning barks. The percentage of tannin in the willow is usually given at from three to five per cent., although Eitner † found over twelve per cent. in several species.

Chestnut-wood.—The wood of the chestnut (Castanea vesca) contains from eight to ten per cent. of a tannin which closely resembles gallotannic acid. The extract, containing from fourteen to twenty per cent. of tannin, is used largely to modify the color produced by hemlock extract and for tanning and dyeing.

Horsechestnut-bark.—The bark of the horsechestnut (Æsculus hippocastanum) is also said to be used for the manufacture of an extract under the simple name of "chestnut extract," but such manufacture in the United States is very doubtful.

<sup>\*</sup>Wagner's Chemical Technology, 13th ed., p. 1051. †V. Höhnel, Die Gerbriende, p. 90.

Catechu (or Cutch) is the name given the dried extract from Acac Catechu, cultivated in India and Burmah, and containing forty-five fifty-five per cent. of a special variety of tannic acid (catechu or mim tannic). The extract is evaporated until a semi-solid dark-brown pr duct is obtained. This is exported in mats, bags, and boxes to Europea and American markets.

Gambier or Gambir (Pale Catechu) is the dried extract from the leaves of Uncaria Gambier and U. acida. It contains thirty-six to for per cent. of a brown tannin which rapidly penetrates leather and tento swell it, but taken alone produces a soft, porous tannage; it is large used in conjunction with other materials for tanning both light an heavy leathers. It is exported from Singapore in pressed blocks at cubes. The catechutannic acids of cutch and gambier differ from gall tannic acid in giving a grayish-green precipitate with ferric salt at no reaction with ferrous salts; by giving a dense precipitate with cupr sulphate and none with tartar emetic. They also contain catechi which is said to be an anhydride of catechutannic acid.

Kino is an extract somewhat resembling cutch, and is the dried juifrom a variety of plants. Thus, the East Indian kino is obtained fro Pterocarpus marsupium, the Bengal kino from Butea frondosa, the African from Pterocarpus erinaceum, and the Australian from the several species of Eucalyptus. It ordinarily forms small angular framents of black lustrous appearance, brittle, and crumbling to brown-repowder. It contains thirty to forty per cent. of a tannin (kinotann acid) analogous to catechutannic acid, together with phlobaphene.

Sumach consists of the powdered leaves, peduncles, and your branches of Rhus coriaria, Rhus cotinus, and other species of Rhu Thus, Sicilian sumach, the most esteemed variety, is from R. coriaria Spanish sumach is from several species of Rhus, and comes in threvarieties, Malaga, Molina, Valladolid; Tyrolean sumach from R. cotinu French from Coriaria myrtifolia; American from R. glabra, R. Can dense, and R. copallina. The leaves are collected while the shrub is full foliage and cured by drying in the sun. They are then groun under millstones and the product baled. The sumach contains from sixteen to twenty-four per cent. of a tannin which seems to be identic with gallotannic acid. The American variety contains usually six eight per cent. more than the European, but also contains more of dark coloring matter, which renders it inferior to the Sicilian sumace for white leathers.

Myrobalans (or Myrabolans).—The fruit of several species of Term nalia found in Hindostan, Ceylon, Burmah, etc. Myrobalans varies is size from that of a small hazel-nut to that of the nutmeg. The tannoccurs in the pulp which surrounds the kernel. It is generally used combination with other tanning materials to modify the objectionab color which some of the latter impart to the leather. By itself it pr duces a soft and porous tannage.

Valonia is the commercial name for the acorn cups of several speci of oak, Quercus agilops and Quercus macrolepis, coming from As Minor, Roumelia, and Greece. They are of a bright-drab color, and contain twenty-five to thirty-five per cent. of a tannin somewhat resembling that of oak-bark, but giving a browner color and heavier bloom. It is generally used in admixture with oak-bark, myrobalans, or mimosabark, because of itself it produces too brittle a leather.

Mimosa-bark (Wattle).—The bark of numerous species of Acacia (A. decurrens and A. dealbata) from Australia and Tasmania, contains from twenty-four to thirty per cent. of mimotannic acid. The bark comes into commerce chopped or ground and also in the form of an extract. It makes a red leather and is generally used in admixture.

Divi-divi.—The seed-pods of Cæsalpinia Coriaria, a small tree found in the neighborhood of Maracaibo, South America. The pods are about three inches long, brownish in color, and generally bent by drying into the shape of the letter S. It contains thirty to fifty per cent. of a peculiar tannin somewhat similar to that of valonia, but is liable to fermentation.

Quebracho.—This is the name applied to several South American trees possessing hard wood. They are Aspidosperma Quebracho (Quebracho blanco), Loxopterygium Lorentzii (Quebracho colorado). The wood and bark of the latter contain from fifteen to twenty-three per cent. of a bright red tannin. Both the wood and the extract are used in tanning.

Nutgalls is the term applied to the excrescences on plants produced by the punctures of insects for the purpose of depositing their eggs. The principal commercial kinds are oak-galls (or Aleppo galls) and Chinese galls. The first of these are the product of the female of an insect called Cynips, which pierces the buds on the young branches of the Quercus infectoria and other species of oak. In the centre of the gall thus produced the larva is hatched and undergoes its transformation, boring its way out as a winged insect in five to six months. If the galls are gathered while the insect is in the larval state they are known as "blue" or "green" galls; if the insect has cut its way out they are known as "white" galls, and are of inferior character and less astringent. The best oak-galls contain from sixty to seventy per cent. of gallotannic acid.

The Chinese gallnuts are the product from the *Rhus semialata*, the leaves of which are punctured by an insect, the *Aphis Chinensis*. The nuts are of irregular shape but are very rich in tannin, containing about seventy per cent.

Knoppern are galls from immature acorns of several species of oak largely used for tanning in Austria. They contain from twenty-eight to thirty-five per cent. of tannin.

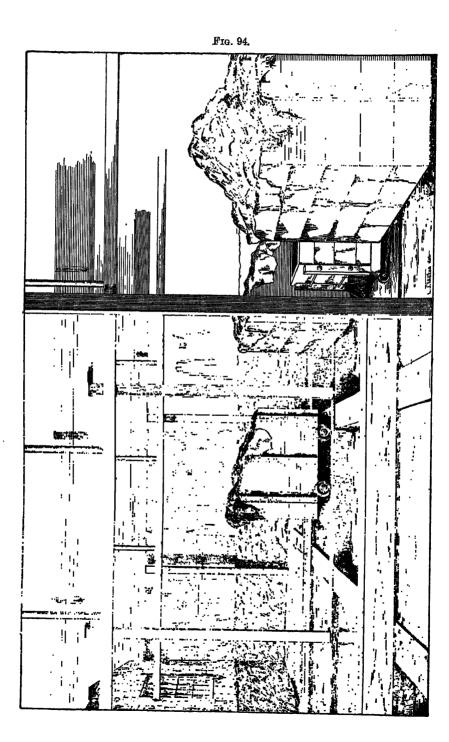
# II. Processes of Manufacture.

Leather may be manufactured from hides or skins by a number of methods, which may be summarized, however, under three heads,—viz., tanning by the use of tannin-containing barks or extracts; mineral tanning, using either chromium salts to make an insoluble leather, or alum

and salt, as in "tawing;" and the manufacture of soft leather by treatment of the skins with oils.

We will note first the methods involving the use of tannin-containing materials, and these again differ somewhat according to the grade of leather to be made and the character of the hides or skins used.

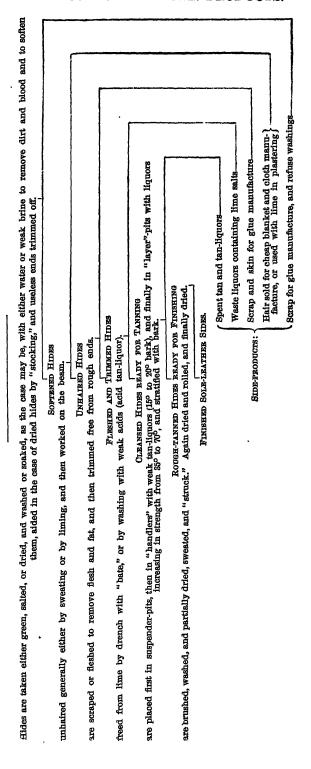
- A. Manufacture of Sole-leather.—1. Softening and Cleansing the Hides.—This process differs according as the hides are taken in the fresh or green state or are salted or dried. For fresh hides, a washing with pure water to cleanse them from dirt and blood is all that is necessary to prepare them for the next or "swelling" process. For salted hides, a soaking in fresh water for from two to three days is necessary, while for hard dried hides a longer treatment is necessary, first in water which has been repeatedly used for softening and afterwards in fresh water. This involves often a slight putrefaction of the coagulated albumen of the dry hide. To control this and prevent injury to the corium of the hide a weak salt solution (five per cent.) is often used in this prolonged softening. "Stocking" or kneading the hides with heavy rolls or breaking weights is also needed for heavy hides which have been dried.
- 2. Unhairing and Swelling .- These operations are carried out together. As the swelling proceeds the cells in which the roots of the hair are embedded are softened, so that the hair is easily removed by mechanical means. The horny epidermis is similarly softened, so that it can be removed by the same means. The swelling may be effected by several different methods: (1) by sweating; (2) by treatment with acid tanliquor; (3) by liming; (4) by treatment with sulphides of sodium and calcium, etc. The sweating process now in use is the so-called "cold sweating" method, and consists in hanging the hides in a moist chamber kept at a uniform temperature of 60° to 70° F. (15° to 21° C.), so that an incipient putrefaction ensues which attacks the soft parts of the epidermis and root-sheaths before materially injuring the corium of leather-forming material. This method is that generally followed for sole-leather in this country and on the Continent of Europe, while in England liming is more generally adopted. The swelling with acid tan liquor depends upon the action of the acids which are present in con siderable quantity in old tan-liquors and their effect upon the connectiv The swelling and unhairing by lime always adopted for smal skins is also used for sole-leather hides in England. A view of the lime pits and skins in process of softening by lime as carried out in morocc tanneries is shown in Fig. 94. The action of the lime upon the hide i in part a solvent one. The hair-sheaths are loosened and dissolved an the hardened epidermis swells up and softens, so that both come awa more or less completely with the hair when scraped. The intercellula substance, or coriin, as before stated, is also soluble in the lime-wate and as this is removed the fibrous nature of the leather-forming sk The hides are generally put into several lim hecomes more evident. pits in succession, in the first of which is old liquor with the weaks alkaline reaction because of its partial saturation with organic materiand in the last the liquor is the freshest and strongest in alkaline res



tion. The hides require to be turned and changed in position during this liming process as well as removed from one pit to the other. The swelling and unhairing by the use of alkaline sulphides largely used upon the Continent of Europe consists in taking a solution of sodium sulphide (made from alkali-waste by Schaffner and Helbig's process) and bringing it to a thin pasty condition with lime. This is then spread upon the hair side of the hides and they are packed together for five to twenty hours, when the loosened hair and sulphide paste are washed off and the hides left in water a time longer to "plump" or swell. Another process uses the sulphide in solution only. The hair having been loosened by one or the other of the means just described, it is to be removed by mechanical means. This is usually done on the "beam," a sloping frame of wood or metal, with a blunt two-handled knife, which pushes the hair downward and away from the workman. After the unhairing, the loose flesh and fat, the latter somewhat saponified by the lime, are next removed from the inner side of the hide by a sharp-edged knife. Hand "fleshing" is in many cases superseded by machine treatment, as the hide must not only be scraped but worked to force out the fat which remains in the loose tissue, as this would impede tanning. The hides after the fleshing are trimmed, and the inferior ends and edges are cut off with a sharp knife. They have still to be freed from the traces of lime which they have absorbed during the lime treatment before they can be put in the tan-liquors. This used to be done for sole-leathers. as it is still done for calf- and goat-skins, by means of "bate," or dung of animals, mixed with water, but that is now almost entirely replaced by the use of dilute acids which shall combine with the lime, when the lime salts so formed are to be washed out. Dilute sulphuric, phosphoric and hydrochloric acids have been used (the latter being best because its lime salt is soluble), as well as the acid tan-liquors containing gallic The organic acids are considered to be safe acetic, and lactic acids. for the hide than the inorganic.

3. Tanning.—The bark or other tanning material must be crushed and then ground to a state sufficiently fine to allow of the extraction o the tannic acid, and yet not so fine as to cause it to cake together in clayey masses. This is accomplished in bark-mills and disintegrators o various kinds, which need not be specially described here. The tar house into which the cleansed and prepared hides or "butts" now com is provided with rows of pits running in parallel lines, which are t contain the butts during the treatment with the tan-liquor. in most cases are first suspended in weak tanning infusions before the go into the first, or "handler," pits. The object of this is to insure the uniform absorption of tannin by the skins before subjecting them t the rough usage of "handling," which in the early stages of the proce is liable to cause injury to the delicate structure of the skin. Durir this suspension the skins should be in continuous agitation to cause tl tannin to be taken up evenly. Both the suspension and the agitatic are accomplished generally by mechanical means. From the suspende the butts are transferred to the "handlers," where they are laid flat

# OUTLINE OF TANNING PROCESS FOR SOLE-LEATHER.



the liquor. They are here treated with weak infusion of bark, con mencing at about 15° to 20° by the barkometer, and are handle This may be do twice a day during the first two or three days. by taking them out, turning them over, and returning them to the same pit, or more generally by running them, fastened together, fro one handler-pit into another. The treatment of the butts in the handle generally occupies about six to eight weeks, by which time the coloris matter of the bark and the tannin should have "struck" through abo one-third of the substance of the skin. Many of the butts will ha become covered, moreover, with a peculiar "bloom" (ellagic acid) i soluble in water. They are now removed to the "layers," in which the receive the treatment of bark and "ooze," or tan-liquor, in progressi stages until the tanning is complete. Here the butts are stratified wi ground oak-bark or valonia, which is spread upon each butt to tl depth of about one inch, and a thicker layer finally on top. The pit then filled up with ooze, which varies in strength from about 35° bark meter at the beginning to 70° at the end of the treatment. For heav tannages six to eight layers are required, the duration of each rangir from ten days at the beginning to a month in the later stages. Each tin the butts are raised they should be mopped on the grain to remove di and loose bloom.

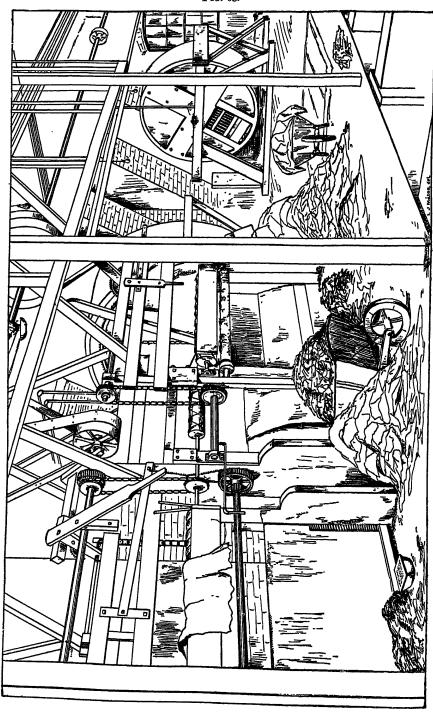
With the use of strong prepared extracts, especially with the aid a heat, the tanning process can be carried out in much shorter time that that just indicated, but the leather produced though hard is deficient i toughness and is liable to crack on bending sharply.

4. Finishing.—The butts after coming from the last layer are we brushed, washed in a clear liquor, and then thrown over a "horse" idrain before going to the drying-shed. They are then frequently oile lightly on the grain so as to prevent too rapid drying out and hung o poles in the drying-loft. When about half dry, they are heaped upon the floor in piles and covered to sweat a little, which facilitates the operation of "striking," which next follows.

The "striking," which may be done by hand with a two-handled to with triangular blunt edges or by machinery, is chiefly for the purpor of removing the deposit called bloom, although it somewhat flattens an stretches the leather. After a little further drying the butt is laid upon a flat bed of wood or metal and is rolled either by heavy hand-rolled or by the aid of machinery. The leather is then sometimes colored to the grain with a mixture of yellow other, with size and oil to give gloss, and then brushed again, well rolled, and dried off gradually in room slightly warmed by steam. The main outlines of sole-leather taining are summarized on the accompanying diagram.

B. Upper and Harness Leathers.—For upper and harness leather the hides of cows and smaller oxen are chosen. Fresh hides are, mor over, much better adapted for this class of leathers than dry salted of dry "flint" hides, as the utmost toughness and strength rather than hardness or weight are to be secured. The hides are cleansed, lime and unhaired very much as already described for sole-leather. They as

Fig. 95.



then "bated" in a bate of hen manure or treated with sour bran-liqu to completely remove the lime from the pores of the skin. The remai ing portions of hair-sheaths and fat-glands are at the same time loosened that they are easily worked out by a blunt knife on the bear This final cleansing process is called "scudding." The action of t "bate" is considered by the best authorities to be a fermentative or and the weak organic acids produced neutralize and remove the lir and at the same time soften the hide by dissolving out the coriin ar probably also portions of the gelatinous fibre. "Stocking" is also use to assist in the softening and cleansing. These lighter tannages are al carried out very largely by the aid of gambier in combination with bar valonia, mimosa, and myrobalans. The tanning liquors are often use at temperatures of from 110° to 140° F. (43° to 60° C.). The finishing of the light leathers requires much care in order to give them the prop softness and strength. They are alternately worked with a stretchin iron, or "sleeker," and rubbed with oil or with a mixture of dégra and tallow.

- C. Morocco Leather.—This is generally made from goat-skin although a cheaper variety is made from sheep-skins. The skins as softened and then unhaired by lime, to which a small quantity of arsen sulphide is often added, whereby calcium sulphydrate and sulpharseni are produced, which assist in softening the hair-sheaths and in givin the grain a higher gloss. A view of the unhairing machines and washin drums of a morocco tannery is given in Fig. 95. They are then bate with a mixture of dog's dung and water, known as the "puer." is often followed by a treatment with bran to aid in removing the lin from the skins. A "seudding" or scraping with a blunt two-handle knife on both the grain and flesh sides then ensues to remove the last portions of lime salts and albuminoid matters. The tanning was for merly done with sumach and gambier, either in revolving paddle "tun blers," as shown in Fig. 96, or according to the English method, b sewing up the skins into bags partially filled with the sumach-liquor an then distended by air and floated in a large vessel of the same liquo The bags are turned over constantly, and afterwards piled up in heap The sumach solution is thus forced through the pores of the skin, an the tanning is rapidly effected. The tanned skins are thoroughly washe and "struck," or scraped and rubbed, until smooth. After thoroug drying they are again struck until thoroughly soft and smooth. sumach tannage has been replaced in this country almost entirely by th chrome tanning, to be mentioned later.
- D. MINERAL TANNING OR "TAWING."—Skins may be converted int a substance resembling leather, although in fact essentially differer from it, by the action of alum and salt. There has been no chemical combination, however, analogous to that formed by the gelatine an tannic acid in the ordinary tanning processes, as the gelatine, alum, an salt can be again separated by treatment with water.

The process of tawing is applied to goat, kid, sheep, and other sma skins. The preliminary operations of steeping, breaking, liming, ur hairing, and fleshing, steeping in bran-water and working on the beam, are essentially the same as have been described already. The skins with the pores cleared of lime and sufficiently opened are then put into a kind of wooden drum or "tumbler," such as is used for washing skins and for treating morocco leather skins with sumach solution. For every two hundred skins some twelve pounds of alum and two and a half pounds of salt with twelve gallons of water are used.

The action is continued for a short time only,—about five minutes. They are then put into an emulsion of yolk of eggs with flour and water, and tramped and worked in this until it has been thoroughly absorbed. The skins are now hung upon poles to dry, after which they are stretched and softened by drawing them to and fro upon the "stake," a blunt steel blade set in upright position.

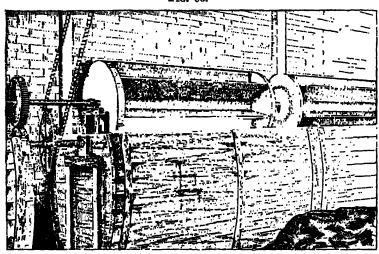


Fig. 96.

"Combination tanning," in which the joint action of gambier and alum is used, is also extensively followed.

Very different from this kind of mineral tanning is that introduced within the last few years under the name of "chrome tanning." It depends upon the power of chromium oxide (sesquioxide of chromium) of forming an insoluble compound with the gelatigenous fibre of the hide, furnishing a product which possesses in a high degree the water-proof character desirable for leather.

The process generally in use at present in this country involves treating the skins at first with a weak solution of bichromate of potash to which sufficient hydrochloric acid is added to liberate the chromic acid (of course pickled skins may be used without the necessity of adding free acid). After the skins have taken up a bright yellow color through their entire texture they are drained and transferred to a bath of sodium thiosulphate, to which some acid is added to liberate sulphurous acid, which reduces the chromic acid to green chromic oxide. The sulphurous acid is at the same time oxidized to sulphuric acid, which liberates a

further portion of sulphurous acid, until the whole of the chromic acid is reduced. Hydrogen sulphide liberated from alkaline sulphides has also been used as the reducing agent for bichromated skins, and still more recently electrolytic hydrogen developed upon the bichromated skin itself. In any case the reduction must take place rapidly, so that the potassium bichromate may be reduced superficially before it can "bleed" or diffuse out of the skins into the water of the reducing bath.

The leather so produced is of a pale bluish-green color, tough and flexible, and thoroughly resistant to water. Indeed, it is this latter property which distinguishes it from all other forms of leather, as the combination of the hide fibre or coriin with the chromium oxide is apparently more stable than its combination with tannin and yields less to boiling water, as has been shown in tests made by Professor Henry Procter, of Leeds. The leather can also be dyed and produced in a variety of colors, but the dyeing must be done before the leather dries, as its water-repellent character is such that once dried it cannot be wetted sufficiently to take up a full color.

Chrome-tanning processes involving the use of chrome alum and other salts of the sesquioxide of chromium as the basis of the tanning vat have been used, but apparently the combination does not take place so readily as where the chromium oxide is obtained in statu nascendi by reduction from the bichromate under the influence of reducing agents. Basic chromium salts, such as the basic chromium chloride, have also been proposed as mineral tanning agents, it being claimed that the dissolved chromium oxide is taken up by the hide-fibre at once and that a single bath only is necessary in this case. Such a basic salt is prepared by dissolving commercial chromium hydroxide (chrome green) in hydrochloric acid, adding sal soda until precipitation of the hydrate begins again. The solution is then nearly neutral, and contains an oxychloride or basic chloride in solution. Common salt is also added to prevent injury to the grain of the leather and to facilitate tanning. After the absorption of the chromium oxide is completed the skins are agitated in water containing suspended carbonate of lime to neutralize all traces of acid. They are then washed and are ready for the fat liquor. At the present time the bulk of the glazed kid made in the United States is chrome-tanned, two establishments in Philadelphia each turning out at present three thousand dozen chrome-tanned goat-skins daily.

Quite recently formaldehyde, applied either as gas or in aqueous solution, has been introduced as a tanning agent, the well-known coagulating power of the formaldehyde on animal tissue causing it to unite with the hide fibre to form an insoluble leather. All grades of leather, from sole leather to light morocco, it is asserted, can be made readily and very rapidly by this treatment. As yet, it is too early to judge conclusively of its quality and durability.

E. CHAMOIS AND OIL-TANNED LEATHER.—The skins tanned in this way are sheep- and calf-skins, and formerly chamois- and deer-skins. The flesh splints of sheep-skins are now generally employed for ordinary wash-leather. If heavy hides are taken, the grain side of the skin is

shaved so that the oil can penetrate easily. The skins receive a thorough liming, so that the coriin is thoroughly removed from between the fibres, making them very soft. A bran-drench follows to remove the lime, and they are worked on the beam. The surplus water having been removed by pressing, while still moist they are oiled with fish, seal, or whale oil (to which some five per cent. of carbolic acid is often added). After being stocked for two to three hours, shaken out, and hung up for onehalf of an hour to an hour to partially dry, they are again oiled and stocked, and this process is repeated until the skins lose their original smell of limed hide and acquire a peculiar mustard-like odor. The later dryings are frequently conducted in a heated room, and when the oiling is complete the skins are piled up, and the oxidation of the oil which has already commenced during the fulling and drying is completed by a sort of a fermentation, in which the skins heat considerably. This heating must be controlled so that the leather is not injured, and if necessary the pile of skins is turned. When the oxidation is complete the skins are of the vellow chamois leather color. To remove the surplus oil, the skins are again oiled, then thrown into hot water and wrung out. The semi-solid fat obtained this way is the dégras so much prized for currying purposes. Or the whole of the uncombined oil is removed by washing with soda or potash lye and then set free by neutralizing with sulphuric The oil so obtained forms the "sod oil" of commerce. About half of the oil employed is retained by the skin, and cannot be removed even by boiling with alkalies. No gelatine is obtained by boiling with water, to which the chamoised skin is much more resistant than ordinary leather. The skins intended for gloves, etc., are bleached like linen, by sprinkling and exposure to the sun or with weak solution of potassium permanganate followed by sulphurous acid.

# III. Products.

- 1. Sole-leather.—This is the heaviest and firmest variety of leather produced. It is made from the heaviest and thickest hides, and is valued for its fine grain and toughness. It retains the whole thickness of the hide, and no part is split off, so that it is not weakened by the loss of the flesh side. The tanning process is protracted until the whole hide is of uniform color throughout and shows the completed action of the tannin upon the interior of the hide.
- 2. UPPER AND HARNESS LEATHERS.—These are made from lighter hides, and are tanned for strength and flexibility rather than for weight, and are finished with care to give perfect pliability. They may be shaved or split leather. The black color and finish are put on upper leather by coating it with a mixture of lamp-black, linseed oil, and fish oil, to which tallow and wax and a little soap have been added. This is brushed on, allowed to dry, and then thoroughly rubbed in and the skin sized with a glue size.
- 3. Morocco Leather.—The true morocco leathers are manufactured from goat-skins. A cheaper grade, known as French morocco, is produced from sheep-skins. As they are to be dyed on one side only, two

of the skins are fixed face to face with the flesh side inward, so the dye acts upon one side of each skin only. After dyeing the skin are rinsed and drained, saturated with linseed oil to prevent too rap drying, and then curried by repeated oiling or waxing and rubbing with a glass "slicker."

- 4. Enamelled or Patent Leathers.—These are leathers finished with a water-proof and bright varnished surface similar to lacquer woodwork. The name "enamelled" is generally applied when the leathers are finished with a roughened or grained surface, and "patent or "japanned," when the finish is smooth. Thin and split hides are use The skins after drying are prepared with a mixture of linseed oil at white lead and heated in closets to 160° F. (71° C.) or higher, the coated with a varnish of spirits of turpentine, linseed oil, thick cop varnish, and asphaltum, and heated again in closets or "stoves," as the are termed. This varnishing and heating are alternated, while the su face is meanwhile rubbed smooth with pumice, until the desired thickne is acquired.
- 5. Russia Leather.—This variety is peculiar in its characterist odor and ability to withstand dampness without any tendency to moulboth of which qualities it owes to the currying with the empyreumat oil of birch-bark. In Russia the skins are tanned with willow-bark, but the imitation Russia leather made largely in Germany and England tanned in the ordinary way with oak-bark. The birch-bark oil is rubbe into the flesh side of the tanned skins with cloths, care being taken not apply so much as to cause it to pass through and stain the grain side of the leather. The red color is given by dyeing with Brazil-wood of red saunders, and the diamond-shaped marking by rolling with groove rollers.
- 6. CHAMOIS LEATHER is a soft felt-like leather originally prepare from the skin of the chamois goat, but now made from other goat-skin and from the "flesh-splits" of sheep-skins. In these leathers the grain has practically been removed by scraping or "prizing" before the oil applied, so that it is uniformly porous and soft throughout. The acquire a yellow color and a peculiar odor, although they are ofte bleached whiter by subsequent treatment. (See preceding page.) The combination of oil with the hide makes chamois leather very resistant to water and allows it to be washed without any change of nature.
- 7. WHITE-TANNED OR "TAWED" LEATHER.—Skins to be tanned wit the hair on, as sheep-skin rugs, etc., are always alum-tawed, as well a light calf kid and glove leather. The glove leather obtained in the process has softness and considerable strength but is not thoroughly water-resistant, although the treatment with egg-yolk and flour-past which follows the alum treatment tends to give it somewhat of this character.

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8. Crown Leather.—This is a variety which is intermediate betwee oil-tanned and tawed leather, being stronger than the first and more water-resistant than the latter. The hides are first tawed with the alunand salt mixture, then washed to partially dissolve out the tawing materials, and now spread upon a table and the flesh side covered with

mixture of fat, ox-brain, barley-flour, and milk. They are then put into a revolving tumbler and rotated for a time, and again rubbed with the fat mixture and rotated if necessary. The leather readily becomes mouldy, but seems to be strong and specially adapted for belting.

- 9. Parchment and Veilum.—The first of these is prepared from the skins of sheep and goats and the second from the skins of calves. The skins are washed, limed, unhaired, and fleshed, again well washed, and then stretched either upon hoops or upon a square wooden frame called the herse. On these the skin while wet and soft is stretched thoroughly. It is then scraped again free from the fleshy matters, the flesh side dusted over with sifted chalk or slaked lime and rubbed in all directions with a flat piece of pumice-stone. The grain side is also scraped with a blunt tool and rubbed with pumice. The skin is then allowed to dry on the frame in the shade, care being taken to avoid sunshine or frost. Very fine vellums are prepared with the finest pumice-stone.
- 10. Dégras.—Among the side-products of the leather industry is one which is quite valuable for after-use. Dégras, originally obtained only as a side-product of the chamois-leather manufacture, is now also made specially on a large scale. The purest dégras is essentially an emulsion of oxidized fish oil produced by soluble albuminoids. That which is squeezed out of the skins after completion of the fermentation and heating, which makes the last stage of the chamois-leather manufacture (see p. 370), is the finest grade of dégras. That which is recovered by the aid of caustic alkalies and after-liberation with sulphuric acid is the second grade (sod oil). The great demand for dégras for currying purposes has led to the manufacture of it as a special industry. The skins employed for this purpose are treated exactly as are those in the normal chamois-leather manufacture, but are used over and over until no longer capable of taking up the oil. An artificial dégras has also been made from oleic acid, fat, and a little lime soap to which some tannic acid had been added.

Dégras is of semi-solid consistence and has a peculiar odor. Its specific gravity is higher than that of fish oil, and after dehydrating is from 0.945 to 0.955. Its characteristic constituent is the so-called dégrasformer, which in a genuine dégras should range from twelve to twenty per cent. It is this which effects the ready emulsion with water. The dégras-former is a brown resinous saponifiable substance, fusing at from 65° C. to 67° C., and is distinguished from fats in that it is not precipitated when in alkaline solution by salt and is not soluble in petroleum-ether. According to Fahrion, the dégras-former is a mixture of oxy-fatty acids.

# IV. Analytical Tests and Methods.

- 1. QUALITATIVE TESTS FOR THE SEVERAL TANNING MATERIALS.—H. R. Procter \* has constructed the following table (see p. 373) showing the reactions of the several tanning materials.
  - 2. Analysis of Liquid and Solid Tanning Extracts.—The method

QI.	Ammoniacal pieric acid solution.	um ace-	Manganese ace-	Cobalt acetate.	Lead nitrate.	Add concen- trated sul- phuric acid to one drop of infusion.	With sodic sul- phide exposed to air on a tile.	Ammonie mo- lybdate in ni- tric acid.	Lime-water.	Add ammonia.	Copper sul- phate.	Add ammonic	Solution of tar-	chloride. Add ammonia.	Bromine-water.	Boiled with equal volume of sulphuric acid (1:9 water).	REAGENT.
Brown pre- cipitate.	No precipi- tate.	ř.; 	ře		Light-yellow	Yellow color.	Yellow color.	Dirty-yellow precipitate.	Yellow pre- cipitate turning greenish	Dense dark precipitate.	Faint cloud- ing.	Light pre-	No precipi-	precipitate. Brown pre-	No precipi- tate. Rina bleak	Pale deposit on cool- ing (ellagic acid).	Myrobalans.
Brown pre- cipitate.	No precipi- tate.	Ä.	ē	Buff-pink precipitate.		Intense crimson.		Dark-green- ish precipi- tate.	Yellow pre- cipitate turning	Dense dark precipitate.		ř	cloud-	4	No precipi- tate.	Pale deposit on cool- ing (ellagic acid).	Divi-divi.
Brown pre- cipitate.	Brown pre- cipitate.	Dark-red			Pale precipi-	Deep yellow.	Turns pur- plish-red.	Dark-green- ish precipi- tate.	Yellow pre- cipitate turning	Dark-red- dish pre- cinitate	No precipi- tate.	Pale precipi-	No precipi-	precipitate. Red-brown	No precipi- tate.	Slight pale deposit.	Valonia.
Brown pre- cipitate.	No precipi- tate.	Dark-brown	Brown pre-	Brown pre-	Brown pre-	Deep-red precipitate on dilu- tion.	Turns red.	Greenish precipitate.	Brown pre- cipitate.	Brown' pre- cipitate.	Slight pre- cipitate.	Whitish pre-	No precipi-	precipitate. Red-brown	Pale precipi- tate.	Slight pale deposit or turbidity on cooling.	Oak-bark,
Brown pre- cipitate.	No precipi- tate.	ŭ	recipi-		Brown pre-	Dark brown.	Reddish pre- cipitate.	Dirty-green precipitate.	Purplish- brown pre- cipitate.	Dark-brown precipitate.	No precipi- tate.	Pale precipi-	Slight cloud-	precipitate. Dull-red	No precipi- tate.	Slight red deposit on cooling.	Chestnut- wood. (Extract.)
No precipi- tate.	No precipi- tate.	lark-	Slight cloud-		Pale precipi-	Dark-brown or crimson.	No change.	Slight cloud- ing.	Dirty-brown precipitate.	Deep-blue coloration.	Slight cloud- ing.	Pale precipi-	No precipi-	precipitate. Dull-red	Yellow pre- cipitate.	Yellow floc- culent de- posit, sepa- rates quickly.	Hungarian larch. (Extract.)
Brown pre- cipitate slowly formed.	Clouding.	Light-brown	Slight pre-	Purple pre-	Pale precipi-	Intense crimson.	No change.	Slight pre- cipitate.	Brown pre- cipitate.	Dark-green coloration.	Pale precipi- tate.	Slight pale	No precipi-	precipitate. Reddened	Yellow pre- cipitate.	Abundant red floccu- lent de- posit.	Hemlock. (Extract.)
Brown pre- cipitate.	No precipi- tate.	Dark-red	No precipi-	Brown pre-	Clouding.	Intense pur- ple-red.	Turns red.	Brown pre- cipitate.	Slight red- dish pre- cipitate.	Deép-red precipitate.	Slight pre- cipitate.	Dense white	White pre-	precipitate. Purple color.	Yellow pre- cipitate.	Heavy red deposit on cooling.	Mimosa- bark.
Brown color.	No precipi- tate.	Dark-red	No precipi-	pre-	ecipi-	Deep red, no precipitate on dilution.	Slight red- dening.	_ O .⊤	Slight cloud- ing, soluble in excess.	ă #	φ.	recipi-	No precipi-	precipitate. Dark-red	Yellow pre- cipitate.	Light-red deposit on cooling.	Cutch. (Pegu.)
Brown precipitate slowly formed.	No precipi- tate.	Dark-red	recipi-	recipi-		Dark brown or crimson.	No change.	No precipi- tate.	No precipi- tate.	Dark-green color.	No precipi- tate.	Faint cloud-	No precipi-	green color. Reddened.	e.	Reddish de- posit on cooling.	Gambier. (Cuba.)
Brown pre- cipitate.	No precipi- tate.	Crimson	White pre-	Purple pre-	White pre-	Yellow.	No change.	Yellow color.	Pale precipi- tate, turns blue.	H	No precipi- tate.	-1	. W_	precipitate. Reddened	No precipi- tate.	Usually some pale deposit.	one per cent.

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prescribed by the "Official and Provisional Methods of Analysis" of the U. S. Department of Agriculture is as follows: Dissolve in nine hundred cubic centimetres of water at 80° C. such a quantity of the extract as will give from 0.35 to 0.45 gramme of tannin in one hundred cubic centimetres of solution. Allow to cool slowly for from twelve to twenty hours at a temperature not below 20° C. and dilute to one litre.

- a. Thoroughly mix the solution, immediately pipette one hundred cubic centimetres into a tared dish, evaporate and dry for sixteen hours in a combined evaporator and dryer at from 98° to 100° C. The result is the total solids.
- b. Add seventy-five cubic centimetres of solution (kept at from 20° to 25° C. during filtration) to two grammes of kaolin (free from soluble salts), stir, let stand fifteen minutes, decant, and discard as much as possible of the supernatant liquid and again add seventy-five cubic centimetres of the tannin solution to the kaolin. Stir and pour immediately on a fifteen centimetre folded filter. Keep the filter full and the funnel and receiving vessel covered. Reject the first one hundred and fifty cubic centimetres of filtrate, evaporate and dry the next one hundred cubic centimetres (which must be as clean as practicable) as before under total solids. The residue is the soluble solids.
- c. Non-tannins.—Prepare a sufficient quantity of hide powder in the following manner: Digest with twenty-five times its weight of water until thoroughly soaked; add three per cent. of chrome alum in solution, agitate occasionally for several hours and allow to stand over night. Wash by squeezing through linen, until the wash water gives no precipitate with barium chloride. Squeeze the hide, using a press if necessary, so that it contains from seventy to seventy-five per cent. of water and determine moisture (twenty grammes is a convenient quantity).

Add to two hundred cubic centimetres of the tannic solution such a quantity of the cut hide as contains from twelve to thirteen grammes of dry hide, shake for ten minutes in a shaker and squeeze immediately through linen, add two grammes of kaolin to the filtrate, stir and filter through a folded filter, returning until clear. Evaporate and dry one hundred cubic centimetres as in previous section. Correct the weight of the residue for dilution caused by the water contained in the cut hide powder. This non-tannin filtrate must not give a precipitate with a gelatine salt solution (one per cent. of gelatine and ten per cent. of salt).

- d. The difference between the weight of the soluble solids and the corrected non-tannin residue is the weight of tannin in one hundred cubic centimetres of solution.
- 3. QUANTITATIVE ESTIMATION OF TANNIN.—Of the numerous processes that have been described for this purpose, the only one generally accepted as capable of sufficient accuracy is Löwenthal's permanganate method. This depends upon the oxidation of the tannin, etc., by permanganate of potash in acid solution in the presence of indigo, which serves as indicator, as its oxidation shows the end of the reaction. As solutions of commercial tanning materials contain other oxidials

matters besides tannins, it is necessary to separate these and titrate second time in order to ascertain the volume of permanganate actuall required by the tannin present. This separation may be effected b digestion with hide-raspings, or more conveniently by a solution of gela tine. In practice, a mixed solution of gelatine and common salt is use to which a small quantity of sulphuric or hydrochloric acid is added Procter has also improved the process by adding kaolin, after the gels tine and salt have removed the tannin, for the purpose of facilitatin filtration.

The special precautions and details of the process as generally practice. tised and as modified by the Commission of German Technical Chemist are given in Allen.\* The results are always stated in terms of crysta lized oxalic acid to which the tannin is equivalent in reducing powe upon the permanganate solution, and are gotten by the aid of the preportion c:(a-b)::63:x, in which c represents the volume of per manganate needed for ten cubic centimetres of decinormal oxalic acid a and b the volume of permanganate needed for the tanning infusion before and after precipitation of the tannin. The shaking method wit chromed hide-powder, as given on the preceding page, is that ger erally used by American leather chemists. It is objected to, however by European chemists, that the shaking introduces abnormal condition so that some of the non-tannins are absorbed and that the result wi vary somewhat with the degree of chroming of the hide-powde: Many workers, therefore, prefer the bell, as proposed by Procter, which is packed with the chromed hide-powder and the shaking is dispense with. The most recent method adopted by the International Associatio of Leather Trade Chemists and officially promulgated by them is found i Trotman's Leather Trades Chemistry, p. 146.†

4. DETERMINATION OF ACIDITY OF TAN-LIQUORS.—A method for th determination of volatile and non-volatile organic acids and the su phuric acid present in acid tan-liquors has been given by Kohnstei and Simand. T One hundred cubic centimetres of the tanning liquor as taken and eighty cubic centimetres distilled off, the residue diluted an again distilled with steam. The acidity of the distillate is determined and the result is the volatile organic acids reckoned in terms of acet To determine the non-volatile organic acids, eighty cubic cent metres of the tanning infusion is treated with three to four gramm of freshly-ignited magnesium oxide and the mixture left for some hou with frequent agitation, when the filtered liquid will be nearly colorle and perfectly free from tannin. The magnesia in solution is determine in an aliquot part of the filtered solution, and will be equivalent to tl total free acids of the liquor exclusive of the tannic acid. portion of the filtrate is evaporated to dryness, the residue gently ignite moistened with carbonic acid water, and dried. It is then boiled wi distilled water and the solution filtered. The carbonate of magnes

<sup>\*</sup> Allen, Commercial Organic Analysis, 2d ed., vol. iii, Part i, pp. 109-116. † Leather Trades Chemistry, S. R. Trotman, 1908, J. B. Lippincott Co., Phila.

Dingler, Polytech. Journ., 256, pp. 38 and 64.

remaining insoluble represents the total organic acids, and can be more accurately determined by converting the magnesia into pyrophosphate and weighing. If these total organic acids be calculated in terms of acetic acid, and the previously found volatile acids, reckoned as acetic, be deducted, the difference represents the non-volatile organic acids. The magnesia remaining in the filtrate from the carbonate of magnesia is combined as sulphate, and when determined gives the sulphuric acid of the original liquors.

5. Analysis of Leather.—It is possible in the case of a leather to determine the percentage of moisture, total fats, water-soluble matter, insoluble fibre, and ash. In the case of mineral tannages, the quantitative determination of the chief constituents of the ash is of special importance. The fats are determined by extraction in a Soxhlet apparatus, as described in a previous chapter, carbon disulphide or petroleum-ether being used as solvent. The dry leather residue remaining after this extraction is digested for some hours with distilled water at 40° C. and then thoroughly extracted by fresh water at the same temperature. The washings are then brought to fixed volume and the residue determined in an aliquot portion. Uncombined tannin may also be determined in this aqueous extract by means of the hide-powder or Löwenthal method. The total ash is obtained by igniting a separate quantity of the leather. This is chipped in small fragments and ignited gradually in small portions in a platinum dish. After the leather swells and carbonizes, it can be burned completely at a dull-red heat without loss of the mineral salts.

# B. GLUE AND GELATINE MANUFACTURE.

Glue is a decomposition product of many nitrogenous animal tissues. These lose on heating with water (analogous to starch-granules) their organized structure, swell up, and gradually go into solution. The solutions, even when very dilute, gelatinize on cooling, forming a jelly, which dries to a horny translucent mass. This mass is glue or gelatine, as the finer grades are termed. It dissolves in hot water to a liquid possessing notable cementing power. Neither the original solution tobtained from the nitrogenous tissues nor the jelly formed from it on cooling have any cementing power. This is only acquired when the jelly has dried to the hard mass known as the glue. Two proximate principles seem to be present as characteristic in all preparations of glue: glutin, obtained chiefly from the hide and larger bones, and chondrin, from the young bones while yet in the soft state and the cartilage of the ribs. and joints. Of these, the former much exceeds the latter in adhesive power, and is therefore sought to be obtained predominantly in the glue manufacture.

# I. Raw Materials.

1. Hides and Leather.—The corium of the animal hides (see p. 356) is the most important glue-yielding material to be had. Neither the epidermis nor the underlying fat-tissue contribute to the glue production, but have rather an injurious effect when present. What is known

as "glue-stock" is made up of the trimmings from the ox, sheep, and calf-skins, the refuse of the beam-house, and scraps of parchment, which have been softened and unhaired by liming and are in condition for-immediate boiling. Of still greater value are the so-called calves' heads, which after liming and drying form a special article of commerce. The amount of glue obtainable from these various materials varies from fifteen to sixty per cent. According to Fleck,\* the scraps from the alum-tawing process yield forty-five per cent., those from the ox-hides thirty per cent., hare- and rabbit-skins and parchment trimmings fifty to sixty per cent., foot and tail pieces of oxen fifteen to eighteen per cent., other scraps from the tanneries, such as ear-laps of sheep and cows, sheep's feet, etc., thirty-eight to forty-two per cent. Scraps of bark-tanned leather, such as shoemaker's and saddler's trimmings, are also available after a special treatment for the removal of the tannin. (See p. 379.)

- 2. Bones.—The bones contain on an average nearly one-third (32.2 per cent.) of their weight of organic constituents, extracted by boiling and converted into glue, which, however, is inferior in adhesive power to that prepared from animal skins. The soft bones of the head, shoulders, ribs, legs, and breast, and especially deer's horns and the bony core of the horns of horned cattle, yield a larger quantity of glue than the hard thigh-bones and the thick parts of the vertebra, which are principally composed of calcium phosphate and require a more prolonged treatment to extract the glue-making constituents.
- 3. FISH-BLADDER.—The inner skin of the air-bladders of the several varieties of sturgeon and cod furnishes a very pure glue substance, which on account of its purity is preferably used for culinary and medicinal purposes, and is known as "isinglass." It is inferior in adhesive power to hide-glue, but on account of its freedom from color, taste, and odor, and its almost perfect solubility in hot water, commands a higher price. It is used for food preparations, for clarifying wine, beer, and other liquids. The chief production of isinglass is from the sturgeon in Russia, on the borders of the Caspian and the Black Sea.
- 4. Vegetable Glue.—Certain species of alge (*Plocaria tenax* and others) found in Chinese and Japanese waters when cleansed and boiled yield a product known under the several names of "Chinese isinglass" and "agar-agar." Of similar character is no doubt the "algin" obtained from Scotch alge by E. C. C. Stanford.

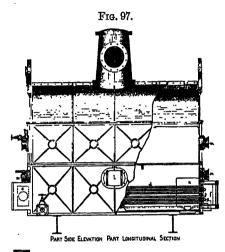
### II. Processes of Manufacture.

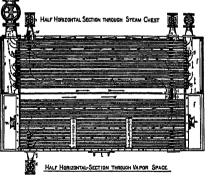
1. Manufacture of Glue from Hides.—The hide trimmings and offal, if in the fresh state, must first of all be well limed,—that is, treated with milk of lime in pits for a period varying from ten to forty days, according to the character and source of the hides, the lime being frequently renewed. The lime softens and swells the hide-tissue, saponifies

<sup>\*</sup> Die Fabrikation Chemischer Producte, etc., p. 60.

<sup>†</sup> Soc. Chem. Ind. Jour., 1884, p. 297.

the fats, and dissolves in large part the coriin, blood, and flesh-particles which do not form glue. The glue-stock is then thoroughly washed free from the lime, lime salts, and dirt, usually by putting it in nets or wicker baskets which are suspended in running water. The liming also serves to preserve the glue-stock in case it is not to be immediately worked up. After washing it is spread out to dry. The lime scum from the pits is often utilized in fertilizer manufacture. Caustic soda has also





been used instead of milk of lime for this treatment. A short treatment with chloride of lime immediately after taking the stock out of the lime-pits has also been found to give the glue a bright color and excellent adhesive power. In recent years sulphurous acid has been used with advantage to cleanse and prepare the glue-stock, as it bleaches and at the same time swells the hide, at least as well as can be done by the lime.

The boiling and conversion of the glue-stock into solution may be effected by heating with water or with steam. The use of steam, either from closed pipes or direct steam from perforated pipes, greatly improves the extraction, shortening the time required and improving the quality of the product. high-pressure Direct steam blown into closed vessels has been found to be quite effective in rapidly melting down the glue-stock and producing a concentrated solution.

The use of vacuum-pans and the extraction by steam under reduced pressure and at lower temperatures has also been found very satisfactory in giving a good product in which the adhesive qualities of the gluten are in no way impaired. A form of vacuum pan designed for the evaporation of thin glue extraction liquors is shown in Fig. 97. The solution must be freed from any melted fat and lime soaps by skimming and from suspended impurities by settling, by filtering through linen bags, or clarifying by the use of bone-black. The addition of alum as sometimes practised has an injurious effect upon the adhesive power of the product. The residue of the glue-stock left unextracted is pressed out, dried, and sold as a fertilizer containing about four per cent. of

nitrogen. The clarified glue solution is poured into shallow woode moulds some six inches in depth, in which as it cools it gelatinizes to brownish-yellow jelly containing from eighty to ninety per cent. (water. The block of jelly is then turned out upon a smooth table, prviously moistened to prevent adherence, and sawed by horizontal wire into thin slabs, which are again cut by vertical wires into strips of the proper width.

The drying of the jelly is one of the most troublesome parts of the whole process, as it must take place rapidly so that the glue-makin material may not spoil, as it is very prone to do while in the jelly form and, on the other hand, the heat should not exceed 20° C. (68° F.). The air is not too moist or too dry, both of which conditions are unfavorable. It is now generally effected in drying-rooms in which a currer of warm dry air at the right temperature is made to circulate. As the surface of the cakes after drying is generally rough and dull, it improved in appearance by moistening with warm water, brushing wit a soft brush, and again drying.

- 2. Manufacture of Glue from Leather-waste.—Before attemping to boil the leather-waste to glue, the removal of all traces of tannacid becomes absolutely necessary, since the retention of the smaller quantity prevents the animal tissue from dissolving in water. The wast must therefore be comminuted as thoroughly as possible to facilitate the complete removal of the tannic acid. This is done frequently in the "hollander" used for paper-pulp, and the washed and ground leather waste then heated in a pressure-boiler under a pressure of two atmospheres with fifteen per cent. of its weight of slaked lime. After the ough washing, the residue is ready for use as glue-stock.
- 3. Manufacture of Glue or Gelatine from Bones.—Two method have been followed for the extraction of gelatine, as the product generally called in this case, from bones. The bones are either boils under pressure, or they are treated with hydrochloric acid to remov the calcium phosphate and afterwards boiled for the extraction of the gelatine. The bones in either case are with advantage deprived of the fat first, which is done either by heating them with water and stea in boiler-shaped vessels, when the fat rises and can be skimmed off fro the water, or in closed vessels with volatile solvents like petroleur benzine and carbon disulphide. The older process of extracting tl gelatine by boiling the powdered bones with water under pressu decomposes a portion of the valuable material, and is now general replaced by the method of treatment with hydrochloric acid for t' removal of the calcium phosphate. The crushed bones are placed wooden vats with dilute hydrochloric acid of specific gravity 1.05 (for litres of acid to ten kilos, of bones) and allowed to remain for sever days. They are then placed in lime-water for a time, well washed, at boiled eight to ten hours with a large excess of water, or converted mo rapidly into gelatine solution by the aid of steam. The resulting sol tion is filtered through cloth, bleached by sulphurous oxide, and pour

into forms to gelatinize. The manufacture of bone gelatine is frequently combined with the fertilizer manufacture, as the calcium phosphate extracted by the hydrochloric acid treatment contains from eighteen to twenty per cent. of phosphoric acid. The newer method of extracting the fat by volatile solvents yields five to six per cent. of fat without injury to the gelatine of the bones, while the older method of boiling out the fat yields from three to four per cent. only and tends to lessen the yield of gelatine.

4. Manufacture of Fish Gelatine.—The swimming-bladders of the fish are taken and thoroughly washed in water from all fatty and bloody particles. They are then removed and cut longitudinally into sheets, which are exposed to the sun and air to dry, with the outer face turned down upon boards of linden or bass-wood. The inner face of the bladders is pure isinglass, which when partially dried can with care be removed from the outer muscular layer. The isinglass layer, possessing a silvery white lustre, is taken either in sheets, rings, or horseshoe-shaped strips, etc., bleached with sulphurous acid, and then thoroughly dried.

A product distinct from isinglass and known as fish glue is prepared by boiling the skin and muscular tissue of fish, and more resembles ordinary hide glue in its adhesive properties, but is offensive in odor. It is prepared from the scales and skins of large fish like the carp by acting on them with hydrochloric acid as upon bones and then extracting with water.

### III. Products.

1. Hide Glue is the variety which shows most strongly the adhesive property, and hence is that manufactured for joiner's and carpenter's use. Its color may vary considerably without any impairing of its adhesive power. It is rarely perfectly colorless or transparent. A gray to amber or brown-yellow color and translucent or partially opaque appearance is more usual. It should be clear, dry, and hard, and possess a glassy fracture. It should swell up but not dissolve in cold water, but dissolve in water at 62.5° C. (144.5° F.). Inorganic substances (such as white lead) are intentionally introduced into some varieties, such as the Russian glue, without injury to their adhesive power.

The variety known as "Cologne glue" is manufactured from scrap hide, which after liming is carefully bleached in a chloride of lime bath and then thoroughly washed.

"Russian glue," as stated, contains some inorganic admixture. It is of a dirty-white color, and contains from four to eight per cent. of white lead, chalk, zinc-white, or barytes.

"Size glue" and "Parchment glue" are both skin glues prepared with special care.

2. Bone Glue (or Bone Gelatine).—Bones yield a product of less adhesive power than the glue of skins and tendons, but when carefully worked the product is clearer and is free from offensive odor. It is

therefore much used for culinary purposes and for medicinal applications, and for fining or clarifying beer, wine, and other liquids it has largely superseded isinglass. The gelatine thus used must, however, be absolutely tasteless and free from odor.

Bone gelatine is now made use of very largely in the manufacture of gelatine capsules, etc., for medicinal uses, of court-plaster for applying to wounds, and of gelatine emulsions with bromide and chloride of silver for coating the photographic dry plates. Mixed with glycerine it makes an elastic mass used for printers' rollers, for hectographs, etc.

"Patent Glue" is a very pure variety of bone glue of deep darkbrown color. It is very glossy and swells up very much in water.

- 3. ISINGLASS (OR FISH GELATINE).—This is the finest and best of animal glues. The best isinglass should be pure white, nearly transparent, dry and horny in texture, and free from smell. It dissolves in water at from 35° to 50° C. (95° to 122° F.) without any residue, and in cooling should produce an almost colorless jelly. The commercial varieties of isinglass are the Russian (the best coming from Astrachan), North American (or New York), East Indian, Hudson's Bay, Brazilian, and German (or Hamburg).
- 4. LIQUID GLUE.—By the action of nitric or acetic acid upon a solution of glue its power to gelatinize may be completely arrested while its adhesive power is not at all interfered with. Thus, if one kilo. of glue is dissolved in one litre of water and .2 kilo. of nitric acid of 36° B. be added, after the escape of the nitrous fumes we have a solution that will not gelatinize on cooling, although it has the full adhesive power of the glue. Four parts of transparent gelatine, four parts of strong vinegar, one part of alcohol, and a small amount of alum will also yield an excellent liquid glue.

# IV. Analytical Tests and Methods.

The nature of glue makes it rather a question of physical and mechanical tests as to quality of a given sample than of chemical tests.

1. Absorption of Water.—Thus the relative amount of water that a given sample will take up when laid in cold water is regarded as a moderately fair criterion of its quality. A weighed sample is laid for twenty-four hours in cold water (not exceeding 12° C. (53.4° F.) in temperature), and at the expiration of that time the excess of water having been poured off, the jelly is weighed. Very good varieties (white gelatine prepared from bones) will take up thirteen times the quantity of water in gelatinizing, second quality glue ten times, and inferior grades only about six times the amount of water. At the same time the consistency of the jelly formed must also be taken into consideration. A firm jelly produced by the absorption of a large quantity of water indicates a glue of the best quality.

Two observations are of value in this connection: first, glue twice dissolved and again dried is capable of drying out more thoroughly and of showing water-assimilating properties on redissolving more fully than glue obtained by a single drying; and, second, that hide glue on taking up smaller quantities of water becomes very soft and more difficult to weigh accurately than bone glue, which, with larger amounts of absorbed water, still forms a firm jelly. This difference in behavior alone is capable of giving an indication of the source of the glue.

- 2. Inorganic Impurities.—The presence of inorganic salts, as in the case of Russian glue, can be determined by the use of the appropriate reagents, and the amount also quantitatively determined.
- 3. Adulteration of Isinglass with Glue.—Isinglass is sometimes adulterated by rolling up sheets of gelatine (bone gelatine) between the layers of true isinglass and drying them in this condition.

Redwood and Letheby have observed that the ash of pure isinglass does not exceed .9 per cent., while glue contains from two to four per cent. of ash. An adulterated sample of isinglass gave Letheby 1.5 per cent. of ash.

On heating with water, true isinglass gives only a peculiar fish or algae odor, while the adulterated isinglass gave a strong glue-like odor at once recognizable.

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### STATISTICS.

### 1. Importations of Tanning Materials into the United States.

1908.	1909.	1910.
Gambier or terra Japonica (pounds)26,681,791	30,992,245	25,572,6
Valued at	\$1,313,997	\$1,255,2
Quebracho extract (pounds)98,186,787	102,004,981	95,183,0
Valued at\$2,260,304	\$2,740,530	\$3,021,9
Quebracho-wood (tons)	66,113	80,2
Valued at \$612,971	\$731,795	\$1,058,6
Sumac (pounds)	10,974,613	13,632,8
Valued at \$227,611	\$293,299	\$299,1

# 2. IMPORTATION OF SKINS AND HIDES INTO THE UNITED STATES.—

1909.	1910.
104.048,244	115,844,758
\$26,023,914	\$30,837,590
48,906,326	67,406,131
\$8,276,637	\$11,289,158
	75,503,451
	\$17,922,051
192,252,083	285,468,821
\$23,795,602	\$42,306,943
	19,512,397
	\$3,080,484
99,347,672	12,258.753
\$20,319,171	\$2,418,414
444,554,325	608,619,028
\$78,487,324	\$112,247,836
	\$26,023,914 48,906,326 \$8,276,637 

### 3. Leather Industry According to Census of 1905.—

3. Leather Industry According to	CENSUS OF 190	5.—
Raw materials used—		
	Number.	.Value.
Hides and skins of all kinds	17.581.613	\$89,126,593
Tanning materials—	,002,020	400,0,0
Hemlock bark (cords)	1,000,328	8,471,292
Oak bark (cords)		3,765,559
Gambier (bales)		752,347
Hemlock extract (barrels)		265,665
Oak-bark extract (barrels)	214,391	2,300,395
Quebracho		2,490,487
Sumac (tons)		338,614
Chemicals		2,847,441
All other materials used in tanning		3,798,244
Oil, degras, tallow, etc., used in currying		3,807,186
Aggregate value of products		252,620,986
Tigging thing of products title	• • • • • • • • • • • • • • • • • • • •	202,020,000
4. United States Exports of Leate	ier.—	
1908	8. 1909.	1910.
Sole-leather (pounds)31,189	,897 33,002,746	38,332,247
Value\$6,593		
Upper leather—		. , ,
Kid, glazed—value 2,879	9,969 3,593,909	10,926,255
Patent or enamelled-value 131	154 168,825	
Splits, buff, grain, and other upper		
leathers—value	2,497 17,623,525	15,620,336
All other leather 2,004	1,022 2,159,542	
	-,	_,,
m 70		
5. Production of Glue and Gelatin	E IN DIFFERENT	COUNTRIES.—
United States (Census of 1905), 50,000 to	one relead at 010	004 605
Germany (1901) 32,000 tons, including 20	ons, varued at \$10,	V34,089.
England (1907), 30,850 tons, valued at \$2	NO POUR OF TIME &	etatine.
England (1907), 50,000 tons, valued at \$2	,530,000.	
6. Exports of Glue and Gelatine i	DOM THE HATTE	Carama
The state of Chor and Children	THOM THE UNITE	D CTATES.
190		1910.
Glue (pounds)2,917	7,173 2,340,426	2,488,205
Valued at\$289	9,441 \$244,751	\$261,756
	•	• •
7 T C		
7. Imports of Glue and Gelatine i	INTO THE UNITE	d States.—

1908.

Glue and gelatine (pounds) .....6,731,943

Valued at ......\$629,032

1909.

6,610,894

\$655,127

1910.

8,821,554

\$861,888

### CHAPTER XI.

### INDUSTRIES BASED UPON DESTRUCTIVE DISTILLATION.

DESTRUCTIVE distillation has been defined as "the decomposition of a substance in a close vessel in such a manner as to obtain liquid products." It must be observed here that the word product is used to ind cate something not originally present in the substance distilled. A bod may be obtained in the liquid distillate which has merely been drive over by heat and which already existed in the original material in physical or mechanical admixture. Such a body is, to speak exactly, a educt and not a product.

The substances which are submitted to destructive distillation are i the main solids, as most classes of liquids are capable when heated wit care of volatilization without decomposition, although such liquids a fatty oils, glycerine, etc., are decomposed if distilled under norms atmospheric pressure. (The cracking of petroleum is another illustra tion of destructive distillation of a liquid purposely brought about. With solids, on the other hand, it is the exception rather than the rul to find one capable of melting and vaporizing unchanged in compositio when distilled under normal atmospheric pressure. The same solic moreover, if of at all complex molecular composition, may decompose quite differently and yield different sets of products according to th conditions which govern the distillation. The most important of thes modifying conditions is that of temperature. "Low temperature" dis tillation and "high temperature" distillation as practised upon th same material (wood or coal, for example) may yield quite differer The physical condition or mechanical subdivision of the sul stance also has an influence, although a subordinate one, upon the natur of the products. Solids, upon the destructive distillation of whic important industries are founded, are wood, coal, shales, bones, an animal refuse. The distillation of shale has already been considered i connection with the mineral oil industry. (See p. 28.) The other in dustries will now be noted in succession.

# A. DESTRUCTIVE DISTILLATION OF WOOD.

### I. Raw Materials.

1. Composition of Wood.—The wood which is to be destructive distilled is composed, we may say in general terms, of woody fibre an plant-juice or sap, which is an aqueous solution of the substances, but nitrogenous and non-nitrogenous, which serve as the food for the livin plant. The woody fibre is made up primarily of cellulose, which is part changed into "lignin," as the incrusting substance is called. I percentage composition this latter substance differs from the pure cell

lose in containing more carbon and less oxygen and hydrogen. The amount of incrusting material varies, being more abundant in hard and heavy varieties than in light and soft kinds, and wood which contains it in the largest proportion gives the most acid and naphtha on distillation. The amount of water present in wood also varies not only according to the season of the year, but also quite widely in different woods cut at the same season. Thus, the following table of Schübler and Hartig shows the percentage of water of different trees taken at the period of minimum amount:

Per cer	nt. of water.	Per cent. of water.
Beech	18.6	Horsechestnut 38.2
Willow	26.0	Pine 39.7
Maple	27.0	Alder 41.6
Elder	28.3	Elm 44.5
Ash	. 28.7	Lime 47.1
Birch	30.8	Lombardy poplar 48.2
White hawthorn	. 32.3	Larch 48.6
Oak	. 34.7	White poplar 50.6
White fir	. 37.1	Black poplar 51.8

2. Effect of Heat upon Wood.—The effect of heat upon wood in the absence of air is a matter which is to be carefully noted as throwing light upon the results obtained in destructive distillation. It of course differs radically from the result of heating with free contact of air. Violette \* found that when wood was carefully and slowly heated no decomposition occurred under 150° C., water only being given off; between 150° and 160° C. the loss was two per cent. of weight of the water-free wood; between 160° and 170° C., 5.5 per cent.; between 170° and 180° C., 11.4 per cent., and so on until at 280° C. 63.8 per cent. of volatile products had been driven off and 36.2 per cent. only of the water-free wood remained in the retort. The products given off in this period of heating between 150° and 280° are the valuable liquid products known as pyroligneous acid (acetic acid and its homologues), wood-naphtha or methyl alcohol, methyl acetate, acetone, furfurol, the mixture of phenols known collectively as "wood-creosote," and all other bodies of empyreumatic and tarry odor. Above 280° C., the decomposition proceeds somewhat differently, hydrocarbons, both gaseous and liquid, being formed. The additional percentage of loss by weight between 280° and 350° C. is only 6.5 per cent. of the water-free wood, but it makes from eighty to ninety volumes of gas. The decomposition continues from 350° to 430° C., when the total loss by weight amounts to eighty-one per cent. of the water-free wood. The products obtained within these limits of temperature are largely solid hydrocarbons like paraffin and high temperature products like benzene and toluene, naphthalene, phenol and cresol. From 430° to 1500° C. the additional loss of weight is only 1.7 per cent. We may sum up these results by saying that three periods may be distinguished broadly for this decomposition of wood by heat: first, from 150° to 280° C., the period of watery acid products; second,

<sup>\*</sup> Dingler's Polytech, Journal, 123, 117.

from 280° to 350° C., the period of gaseous products; and, third from 350° to 430° C., the period of liquid and solid hydrocarbons. Violett found also great difference in the results according as the temperatur was slowly raised or as the wood was rapidly brought up to a higher heat. Thus, one hundred parts by weight of wood slowly heated so the the temperature of 432° C. was only reached after six hours left 18.8 parts of charcoal, while one hundred parts of the same wood put into retort previously heated to 432° C. left only 8.96 parts by weight charcoal.

# II. Processes of Manufacture.

1. DISTILLATION OF THE WOOD.—The primitive method of distillin wood devised by the charcoal-burners, in which the wood was piled up i large heaps covered in by clay and turf so as to form a circular domshaped mound, is still followed in some heavily-wooded districts. course the charcoal is the only product sought in this case, and the gas ous and liquid products of the distillation are allowed to escape. I Russia and Sweden the charcoal-burning in mounds is now frequently combined with the collection of tar, which as it condenses is made t flow through inclined troughs, and is drawn off from below. way the valuable birch-bark tar (see p. 371) and kienoel (Russian tu: pentine oil) are obtained. For a proper collection of all the produc of the destructive distillation of wood, however, it is essential that the distillation be carried out in retorts provided with proper condensation These retorts may be either set in horizontal or vertical position, and may be either fixed or capable of removal for emptying and recharging. It is found convenient in large works where it desirable to carry on the distillation continuously to have a series ( retorts connected with one and the same condensation apparatus an heated by the same flues. This arrangement allows of the removal an re-charging of a single retort without interrupting the working of th others. In recent years the American and Canadian wood distillin plants have been built with large horizontal retorts of such size the material in wagons of light skeleton construction can be run in on track prepared for them and the wood distilled without having to hand it until completely changed to charcoal. Several such wagons, each con taining one cord of wood cut to suitable length, are run in one back ( the other, and the doors of the horizontal retort closed and locked tigh when the heating is begun. When the distillation is finished these ca containing the glowing charcoal are pushed from the farther end of the retort into large cooling chambers of boiler iron, where they remauntil cooled sufficiently to allow of their being brought into the a without ignition. The heating should be conducted slowly at first: that the maximum yield of the low temperature products, acetic ac and methyl alcohol, may be obtained, then increased until the gas com off freely, and at the end of this stage of the decomposition aga strengthened to drive over the high temperature products characterist of the last period of distillation. As the maximum temperature need is beyond the record of the mercury thermometer, a pyrometer can be used or a small bar of metallic antimony which melts at 432° C. taken Superheated steam has also been used as a means of accurately controlling the application of heat in the distillation, and it is said that the majority of European works manufacturing charcoal for gunpowder purposes use this method of distillation. The liquid which runs off from the condenser is at first wax-yellow in color, but becomes dark-colored, reddish-brown, and eventually nearly black and quite turbid. When allowed to stand at rest it soon separates in two sharply distinct layers,—the lower one of a thick tar, dark or perfectly black in color, and the upper one, which is much the larger in amount, is the crude pyroligneous acid and is reddish-yellow or reddish-brown in color. A light film of oil often covers, in part at least, this watery layer and represents the benzene hydrocarbons produced. We have already noted the fact that the yield of liquid products is affected greatly by the temperature used for distillation. Different varieties of wood also vary somewhat in the results obtained, even when distilled under the same conditions of temperature. This is illustrated in the following few examples: \*

	Charcoal.	Tar.	Crude pyro- ligneous acid.	Containing actual acid.	Gases.
Red beech { slowly heated rapidly heated	26.7	5.9	45.8	5.2	21.7
	21.9	4.9	39.5	3.9	33.8
	29.2	5.5	45.6	5.6	19.7
	21.5	8.2	89.7	4.4	85.6
	34.7	8.7	44.5	4.1	17.2
	27.7	8.2	42.0	3.4	27.0
	80.8	4.4	41.0	2.7	24.4
	24.2	9.8	42.0	2.4	24.1

Beech-wood and foliage trees in general yield distinctly more acid than coniferous trees, but the latter yield more tar of terebinthinate character. The figures given above, it must be remembered, however, were gotten in experiments with small portions. In practice, working with larger quantities, the yield of several of the products is notably larger. The yield of wood-spirit, or methyl alcohol, varies from five-tenths to one per cent. of the weight of the dry wood.

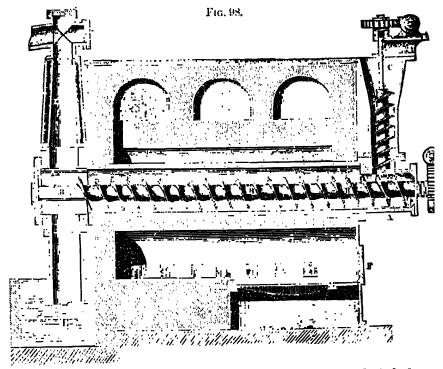
The emptying of the retorts, if done as intended while the charcoal is yet glowing, involves the use of air-tight pits into which the charcoal can be emptied from the retorts and immediately covered with moist charcoal-powder to prevent loss by combustion. A form of apparatus for distilling the sawdust so abundantly produced in wood-working processes has been devised by Halliday, of Salford, England, and is said to work satisfactorily in practice. It is shown in Fig. 98. It consists of a horizontally placed cylindrical retort, A, within which revolves an endless screw, B. The sawdust is regularly fed in through the vertical pipe C, and falling upon the screw is kept moving at a uniform

<sup>\*</sup> Ost, Lehrbuch der technische Chemie, p. 294.

speed along the entire length of the heated retort. At the farther end the vapors and gaseous products of the distillation escape through an ascending pipe, K, leading to the condenser, while the powdered charcoal drops through the pipe D into water, where it is at once quenched.

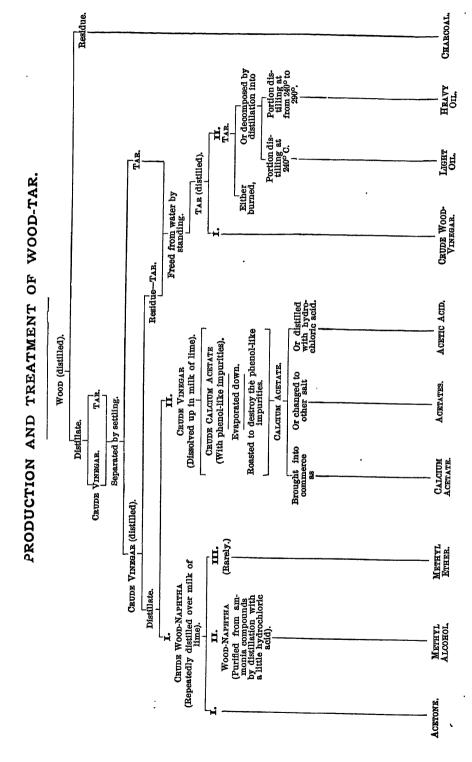
A general view of the products of the distillation of wood and their subsequent treatment is given in the accompanying diagram taken from Post.\*

2. TREATMENT AND PURIFICATION OF THE CRUDE WOOD-VINEGAR.— The brown aqueous solution poured off from the tarry layer (see above) has a strong empyreumatic odor, and contains, besides the acetic acid.



methyl alcohol, acetone, and homologous ketones, allyl alcohol, homologues of acetic acid (such as formic, propionic, butyric, and valerian acids), methyl acetate, acetate of ammonia and of methylamine, ald hyde, furfurol, phenols, and other empyreumatic and tarry bodies. is not used in its crude condition except in the preparation of the cruc pyrolignite of iron (iron-liquor) or in limited amount for impregnatir wood. The first step towards purification is to separate the woodnaphtha (the fraction containing the methyl alcohol, acetone, and methy acetate) from the wood-vinegar (crude acetic acid), which is done the distillation. Two procedures are possible here. Either to neutrali the crude pyroligneous acid with milk of lime and then distil off the volatile constituents only, using an iron still, or to distil the crude pyr

<sup>\*</sup> Post, Chem. Technologie, p. 78.



ligneous acid from a copper still without neutralizing with lime. In the former case, while the wood-naphtha distils off, the tarry impurities of the crude pyroligneous acid remain with the lime salt in the still, and of evaporation a dark mass is obtained known as "brown acetate of lime. In the latter case, after catching the wood-naphtha distillate, the receive is changed and the crude acetic acid is also collected freed to a considerable extent from the tarry matter, so that on neutralizing with mil of lime and evaporating the product is a lighter salt known as "graacetate of lime." The latter process is now more generally in use. The solution of the calcium acetate is evaporated in iron pans; the phenol and tarry products which volatilized with the acetic acid separate largel as seum and may be skimmed off, so that the residue of the evaporatio is much purer than the product of the other method mentioned above.

If the brown acetate of lime has been obtained and is to be further worked for acetic acid, it is found necessary to roast it at a temperatur not exceeding 250° C. so as to drive off as much of the tarry impurit as possible without decomposing any of the acetate. If, on the other hand, the gray acetate is taken, it is distilled from copper retorts wit concentrated aqueous hydrochloric acid, taking care to avoid an excess The acetic acid distils over between 100° and 120° C., is clear in colc and has only a slight empyreumatic odor. Its specific gravity usuall ranges from 1.058 to 1.061, and it contains about fifty per cent. of pur acetic acid. If some water is added with the hydrochloric acid so the the distilled acetic acid is more dilute, it tends to give a purer product as the liberated acetic acid cannot decompose any of the calcium chlorid before coming over. A good proportion is said to be one hundred part of acetate of lime, ninety to ninety-five of hydrochloric acid of 1.16 specific gravity, and twenty-five parts of water. The acetic acid s obtained has a slight empyreumatic odor. It may be freed from this b distilling with from two to three per cent. of potassium bichromate, c by filtration through freshly ignited wood charcoal.

The brown acetate of lime usually contains about sixty-eight 1 sixty-nine per cent. of pure acetate, while the gray acetate contains from eighty-five to eighty-six per cent. of true acetate.

In recent years it has been found practicable to prepare pure acet acid from the crude pyroligneous acid by making the sodium salt in stead of the lime salt. The sodium salt allows of purifying by recry tallization, and can also be fused without decomposition. Glacial acet acid is generally made by distilling the anhydrous and fused sodiu acetate with concentrated sulphuric acid.

Rohrmann has recently developed a process by which it is possib to make ninety per cent. or even glacial acetic acid direct from the cruc acetate of lime in one operation. He uses a column still provided wire Lunge-Rohrmann plates, over which concentrated sulphuric acid is made to trickle. This meets the ascending acetic vapors and dehydrates then They pass over into a condenser, while the empyreumatic vapors a drawn off by a warm-air current which connects with the column. Whe hydrochloric acid is used to decompose the acetate the resulting acet

acid can be brought to eighty per cent.; when sulphuric acid is used, one hundred per cent. acid can be obtained.

- 3. Purification of the Crude Wood-spirit.—The wood-spirit forms the first fraction when the crude pyroligneous acid is distilled, and amounts to perhaps one-sixth of the latter in bulk. It is usual to collect, however, until the hydrometer reading of the distillate, which begins at about .900, has risen to 1.000 or a little beyond. This distillate forms a greenish-vellow liquid of unpleasant odor and contains many impurities besides the acetone and methyl acetate, the chief substances which are present with the methyl alcohol. Milk of lime is first added and allowed to stand with the liquid for several hours. The mixture heats up quite distinctly as the lime combines with any free acid and begins to decompose the methyl acetate and other ethereal compounds of acetic acid. small quantities of ammonia often being given off. It is then distilled by connecting it with a column rectifying apparatus. (See p. 244.) The distillate thus obtained, of about .816 specific gravity, is colorless at first but gradually darkens in color, and if diluted with water becomes milky from separated oily hydrocarbons and ketones. It is therefore diluted down with water to about .935 specific gravity and allowed to stand until this oily impurity rises to the top in a distinct layer. diluted spirit is again distilled over lime once or twice with a rectifying column and so brought to ninety-eight or ninety-nine per cent. strength. The acetone impurity, however, is not removed by any of these rectifications, as the boiling-points of acetone (56.4° C.) and methyl alcohol (55.1° C.) do not allow of their separation in this way. To remove the acetone a number of methods have been proposed. The methyl alcohol may be converted into the solid chloride of calcium compound, or the oxalate of methyl and the acetone having been removed by careful heating, the methyl compound is decomposed by water or alkali. Or the methyl alcohol is distilled over chloride of lime, which reacts with the acetone to form chloroform. The passing in of chlorine in order to convert the acetone into high-boiling chloracetones, which are then separated from the methyl alcohol by distillation, has also been proposed.
- 4. TREATMENT OF THE WOOD-TAR.—The tar which has separated from the crude pyroligneous acid by settling, and that which has risen and been skimmed off in the neutralizing of the acid, are united and submitted to distillation in horizontally-placed iron retorts, which are set at a slight inclination. At first acid-water comes over, then light oils, and finally heavy oils until no more will distil. The pitchy residue is run out while hot, so that it does not adhere to the walls of the retort. The relative amounts of the several fractions from the tar depend upon the nature of the wood used in the original distillation and upon the way that distillation has been carried out. Hard woods usually give a tar which, according to Vincent, when redistilled yields as follows:

The oily distillates are washed with weak soda to remove adhering acid and then carefully rectified, when the oils coming over under 150° C. are collected for solvent and varnish-making purposes, those between 150° and 250° C. collected as creosote oils, and those above 250° C. used for burnings oils.

The creosote oil, which is the most valuable part, is thoroughly agitated with strong caustic soda solution, the aqueous layer drawn off, mixed with sulphuric acid, and allowed to stand for a time at rest, when the creosote oil separates out. This is best driven off by steam distillation and again rectified finally from glass retorts.

Stockholm tar, so largely used in ship-building, is the product of a rude distillation of the resinous wood of the pine.

North Carolina pine-tar is also the product of a distillation of the pine. The billets of pine-wood are piled in heaps like a charcoal-burner's mound, though not so large, covered in with clay and turf, and lighted from the top. The resin or tar distils downward and runs off through inclined troughs previously fixed for it. It is obvious that the composition of both the Stockholm and the North Carolina tar differs notably from that of wood-tar distilled in retorts from hard woods. This composition will be referred to later.

#### III. Products.

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1. Pyroligneous Acid and Products Therefrom.—The crude acid as obtained in the distillation is a clear liquid of reddish-brown color and strong acid taste, with a peculiar penetrating odor described as empyreumatic, and now known to be due largely to the furfurol it contains. It possesses a specific gravity of from 1.018 to 1.030 and contains from four to seven per cent. of real acetic acid. Pyrolignite of iron (iron or black liquor) is a solution of ferrous acetate with some ferric acetate, prepared by acting upon scrap-iron with crude pyroligneous acid. It forms a deep-black liquid, and is concentrated by boiling to 1.120 specific gravity, when it contains about ten per cent. of iron. It is extensively used by calico-printers. Brown and gray acetate of lime have been already referred to. Other technically important acetates are lead acctate (sugar of lead), used in the preparation of the alum mordants and the lead pigments; copper acetate, the basic salt of which is known as "verdigris:" aluminum acetate, the solution of which is used in calicoprinting under the name of "red liquor."

Pure acetic acid is a colorless acid liquid with pungent smell and taste. It crystallizes when chilled in large transparent tablets, melting at 16.7° C., whence the name "glacial acetic acid." Its specific gravity at 15° C. is 1.0553, and it boils under normal pressure at 119° C.

2. METHYL ALCOHOL AND WOOD-SPIRIT.—As before stated, crude wood-spirit is a complex liquid and contains many impurities. The percentage of real methyl alcohol may rise to ninety-five per cent., but more generally ranges from seventy-five to ninety per cent. Some impure wood-naphthas go much lower, however, than this. A large percentage of acetone does not interfere with its use as a solvent for resins and for

varnish-making, but does interfere with its use in the aniline-color industry, where a very pure methyl alcohol is needed for the manufacture of dimethyl aniline. The methods of freeing methyl alcohol from the two chief impurities, methyl acetate and acetone, have already been referred to. Pure methyl alcohol has a purely spiritous odor, a specific gravity of .7995 at 15° C., and boils at 55.1° C. It is miscible in all proportions with water, ordinary alcohol, and ether.

- 3. ACETONE.—This substance is of interest as always produced in the distillation of wood, and hence present in the crude wood-spirit. acetates yield it as the chief product when submitted to dry distillation, and the vapors of acetic acid distilled over porous baryta at a temperature of from 350° C, to 400° C, it has been found by Dr. Squibb, will also readily yield acetone. One hundred kilos, of forty per cent, acid will give from twelve to thirteen kilos. of acetone. At present it is made on a large scale by distilling the gray acetate of lime in iron stills provided with mechanical agitation at a temperature of about 290° C. When purified, it is a colorless liquid of peculiar ethereal odor and burning taste, and, like methyl alcohol, is miscible in all proportions with ether, alcohol, and water. It is an excellent solvent for resins, gums, camphors, fats, and pyroxyline, or gun-cotton. It does not form a compound with dry calcium chloride and can thus be separated from methyl alcohol when in admixture with this latter. Chlorine and iodine in the presence of an alkali react with acetone to form chloroform and iodoform.
- 4. CREOSOTE.—Wood-tar creosote is a strongly refracting liquid, which is colorless when freshly distilled but gradually acquires a yellow or brown color. It has a smoky aromatic odor, which is very persistent and is quite distinct from that of carbolic acid. It has a specific gravity ranging from 1.030 to 1.080, and boils between 205° and 220° C. It is a powerful antiseptic, and is largely used to preserve meats, etc. It differs from coal-tar creosote in containing relatively little common phenol (carbolic acid) and relatively large amounts of higher phenols, such as phlorol,  $C_8H_0.OH$ , guaiacol,  $C_7H_7O.OH$ , and ereosol,  $C_8H_0O.OH$ .
- 5. Paraffin.—This mixture of solid hydrocarbons, as already said, occurs in the higher boiling distillate gotten from wood. It is of interest to recall that paraffin was first discovered by Reichenbach in beech-wood tar. At present, however, the extraction of paraffin from wood-tar is not to be thought of because of the cheapness of its production from petroleum and bituminous shales. It has been already described under the chapter on Petroleum. (See p. 33.)
- 6. Charcoal.—We have already shown in the table of results of slow and rapid distillation of wood (see p. 388) that the relative amount of charcoal depends upon the manner of heating, being larger with gradual application of heat and smaller with rapid heating. The properties and chemical composition of the charcoal are similarly dependent upon the temperature to which the wood is heated. Wood is stated to become brown at 220° C., at 280° C. it becomes a deep brownish-black and begins to be friable, and at 310° C. forms an easily friable black mass taking fire easily. That prepared at higher temperatures is harder and less readily ignited, and it eventually becomes graphitic and rings.

with a metallic sound when struck. The accompanying table from Vic lette shows the gradual change in the composition of charcoal prepare at different temperatures from the same kind of wood (buckthorn):

	Heated to	Carbon, per cent.	Hydrogen, per cent.	Oxygen, nitro- gen, and loss.	Ash, per cent.
Dry wood	150° C.	47.51	6.12	46.29	0.08
	280° C.	67.85	5.04	26.49	0.56
	280° C.	72.64	4.70	22.10	0.57
	820° C.	73.57	4.83	21.09	0.52
	840° C.	75.20	4.41	19.96	0.48
	482° C.	81.64	1.96	15.25	1.16
	1500° C.	96.52	0.62	0.94	1.95

## IV. Analytical Tests and Methods.

1. Assay of Pyroligneous Acid and Crude Acetates.—The crud pyroligneous acid, as before stated, contains from four to seven per cent of real acetic acid. Its strength may be ascertained by titration wit standard alkali, using phenol-phthalein as an indicator. If the liquid i too dark to allow of the end reaction being readily seen, it can be dilute sufficiently, as the reaction will still be sufficiently delicate. In the absence of sulphates in the sample, the acetic acid can be determine by adding excess of pure precipitated barium carbonate to the solution filtering, and determining the barium in the filtrate by the aid of sulphuric acid.

As the pyroligneous acid is largely converted into calcium acetate i the process of purifying, the analysis of the brown or gray acetate o lime as a common cemmercial product becomes of some importance. This commercial acetate may contain from sixty-five to eighty per cent. o true acetate of lime, with carbonate of lime, so-called "tar-lime," an empyreumatic matter as chief impurities. The acetic acid determinatio may be made by different methods, but the most accurate according t the experience of the author is the distillation method, as suggested b Stillwell and Gladding. One gramme of the sample of acetate of lime : placed in a small distillation bulb or flask with a long neck, a litt' distilled water added, and then a solution of five grammes of glacia phosphoric acid dissolved in ten cubic centimetres of water. The flas is then heated to distil off the acetic acid, care being taken to avoi spurting and mechanical carrying over of any of the phosphoric acid When the contents have nearly gone to dryness, some twenty-five cub centimetres of distilled water are introduced and the distillation r peated. If this is done some three or four times, the distillate will ! found to be free from acid reaction. The combined distillate is the brought to definite volume and titrated with decinormal soda solutio using phenol-phthalëin as indicator.

2. Determination of Methyl Alcohol in Commercial Woo spirit.—But one method, and that not capable of the most accura working is at present available. Five cubic centimetres of the samp

of wood-spirit are allowed to drop slowly upon fifteen grammes of phosphorus di-iodide placed in a small flask of some thirty cubic centimetres capacity. This is connected with an inverted condenser and cooled externally while the reaction takes place. Five cubic centimetres of a solution of one part iodine in one part of hydrogen iodide of 1.7 specific gravity is then added and the mixture gently digested for a quarter of an hour, when the condenser having been turned downward the iodide of methyl formed is distilled off. It is collected in a graduated tube divided into one-tenth cubic centimetres, washed with some fifteen cubic centimetres of water with vigorous agitation, allowed to settle, and the volume read off. Five cubic centimetres of pure and perfectly dry methyl alcohol should give 7.45 cubic centimetres of iodide of methyl.

- 3. DETERMINATION OF THE ACETONE IN COMMERCIAL WOOD-SPIRIT.— This may be done by either the Kraemer and Grodzki gravimetric method or the Messinger volumetric method, both of which depend upon its quantitative conversion in the presence of iodine and caustic alkali into iodoform. In the former case, one cubic centimetre of the sample of wood-spirit is mixed with ten cubic centimetres of a double normal solution of caustic soda (eighty grammes to the litre), and to the mixture, after thorough agitation, is added five cubic centimetres of a solution containing two hundred and fifty-four grammes of iodine and three hundred and thirty-two grammes of potassium iodide to the litre. The iodoform which separates on agitation is dissolved by the addition of ten cubic centimetres of ether free from alcohol. An aliquot portion of the ethereal layer is then pipetted off into a tared watch-crystal, and the iodoform remaining after evaporation is weighed. Three hundred and ninety-four parts of iodoform correspond to fifty-eight parts of acetone. More accurate is the Messinger volumetric process. In this, twenty cubic centimetres (or thirty cubic centimetres in samples rich in acctone) of normal potash solution and one or two cubic centimetres of the woodspirit in question are shaken together in a stoppered 250-cubic-centimetre flask and a known quantity (twenty or thirty cubic centimetres) of a one-fifth normal iodine solution added. The mixture is shaken until the supernatant liquid clears perfectly on momentary standing, hydrochloric acid of 1.025 specific gravity is added in amount equal to the potash solution before used, and excess of decinormal sodium thiosulphate run in. Starch paste is then added, and the excess of sodium thiosulphate titrated with one-fifth normal iodine solution. If r be the volume in cubic centimetres of the iodine solution required to combine with the acetone, and n the volume in cubic centimetres of the methyl alcohol taken, then the quantity of acetone by weight in one hundred cubic centimetres of the sample is equal to  $r \times .193345$
- 4. QUALITATIVE TESTS FOR WOOD-TAR CREOSOTE.—The U. S. Pharmacopæia gives the following tests as enabling one to distinguish between wood-tar creosote and coal-tar creosote:
- 1. On stirring together equal volumes of wood-tar creosote and collodion in a dry test-tube no permanent coagulation should form.

- 2. If one volume of creosote be mixed with one volume of ninety-fr per cent. glycerine, a clear mixture will result from which a creosotic lay equal to or greater in volume than the creosote employed will separa on the addition of one-fourth volume of water.
- 3. On adding to ten cubic centimetres of a saturated aqueous soltion of creosote one drop of ferric chloride test solution, the liquid develops a clear violet-blue color, which is very transient; it then cloud almost instantly, the color passing rapidly from a grayish-green into muddy-brown, with finally the formation of a brown precipitate.
- 4. If one cubic centimetre of creosote be cautiously and gently shake with two cubic centimetres of petroleum benzine and two cubic cent metres of freshly-prepared barium hydroxide solution until a unifor mixture is produced, upon complete separation three distinct layers a visible, the middle one of which contains the creosote, unaltered in a pearance; while the petroleum benzine should not be blue or muddy an the aqueous layer should not have acquired a red tint (absence of corn lignol and other high-boiling constituents of wood-tar).

#### B. DESTRUCTIVE DISTILLATION OF COAL.

#### I. Raw Materials.

Probably the most important industry involving the destructive di tillation of coal is the manufacture of illuminating gas. The classes coals employed for the purpose are confined to those varieties whice are bituminous in their nature, yielding when distilled volatile hydrocarbons in varying quantity. The uncombined or "fixed carbon," with the mineral constituents originally present in the coal, remaining after the distillation comprise coke.

Bituminous Coals have the property, not possessed by the anthr cites, of softening and apparently fusing when subjected to a temper ture below that at which combustion would take place. This fusic indicates the commencement of destructive distillation, when both soliliquid, and gaseous carbon compounds are formed. Bituminous coal essentially a coking coal, and as such is, to a very great extent, employe in the coking regions of Western Pennsylvania. It is black or grayisl black in color, of a resinous lustre, and somewhat friable, being easil broken into cubical fragments of more or less regularity; upon ignitic it burns with a yellow flame. When it is heated to bright redness i retorts or ovens, free from the access of air, the volatile matter, befor mentioned, carbon compounds of hydrogen and of oxygen, with wate pass off. Coals having a large percentage of hydrogen will yield mo: volatile substances at the temperature of distillation and less carbon: ceous residue than others which may contain less hydrogen and moi carbon,—approaching anthracite in composition.

Coking and Non-coking Coals are quite similar in chemical compostion; the coking varieties contain less volatile matter, however, than the non-coking; the latter do not possess the property of fusing to a corpact "coky" mass, but retain their original form, and yield a coke which

has no commercial value unless it is obtained from large pieces of the coal.

Cannel Coal is much more compact than gas or coking coals, duller in appearance, possessing a grayish-black to brown color, and burning with a clean candle-like flame. It does not soil the hands, and is not readily fractured. It is capable of taking a high polish, and can be cut or turned into articles for use or ornamentation. Cannel coal occurs in large quantities in West Virginia, and near Glasgow, Scotland, in Lancashire, England, and at other localities. Destructively distilled, it yields a larger amount of volatile matter and ash, with much less coke, than the bituminous coals.

Brown Coal, or Lignite, appears to occupy an intermediate position between the bituminous coals and wood. It retains the ligneous structure of the material from which it is formed,—hence the name Lignitc. The vegetable remains in a great many cases are quite distinct. color varies from yellowish-brown in the earthy, to black in the more compact, coal-like varieties. The percentage of carbon contained is low, fifty to eighty per cent., though rarely exceeding seventy per cent., while the hydrogen is from 4 to 6.85 per cent. Oxygen and nitrogen are present in variable quantities from 7.59 to 36.1 per cent. The ash in good qualities is low, in earthy specimens is high, in many cases exceeding fifty per cent. Lignite does not yield coke. Aside from being utilized as fuel in the several localities where it is found, for both domestic and industrial purposes, it has been distilled for volatile constituents in Saxony.

Peat, or Turf, occurring in large areas in Ireland and in some parts of Europe, consists of the decayed remains of certain forms of plants. It has been, according to Mills, destructively distilled for tarry products, the industry, however, being no longer profitable.

The following tables, taken from the Reports of the Second Geological Survey of Pennsylvania, show the analyses of some of the more important varieties of American gas coals, coking coals, and non-coking, or block coals.

	WESTMOR	ELAND COAL	Company.	PENNSYLVANIA GAS COAL COMPANY.				
	South Side Foster Mine.		Larrimer, No. 2.	Irwin, No. 1.	Irwin, No. 2.	Sewickley.		
Water at 225°. Volatile matter . Fixed carbon . Sulphur	1.410 87.655 54.489 0.686 5.860	1.810 87.100 55.004 0.636 5.950	1.560 89.185 54.352 0.648 4.260	1.780 85.860 59.290 0.680 2.890	1.280 88.105 54.383 0.792 5.440	1.490 37.153 58.193 0.658 2.506		
Total	100.000	100.000	100.000	100.000	100,000	100.000		
Coke, per cent Fuel ratio	60.985 1:1.47	61.590 1:1.48	59.255 1:1.38	62.860 1:1.67	60.615 1:1.42	61,357		

1:1.42

McCreath.

1:1.56

I. Gas Coals.

### DESTRUCTIVE DISTILLATION

II. Coking Coals.

				<b>W</b>	*	
	Connells- ville, Frick & Co.	Bennington, Cambria Iron Company.	Broad Top, Barnet.	Broad Top, Kelley.	BAN land.	County,
Moisture Volatile matter . Fixed carbon . Sulphur Ash	1.260 30.107 59,616 0.784 8.238	1.400 27.225 61.843 2.602 6.930	16.00 74.65 1.85 7.50	19.68 71.12 1.70 7.50	1.10 15.80 73.28 1.28 9.08	0.250 14.510 77.042 1.838 6.860
Total	100.000	100,000	100.00	100.00	100.00	100.000
Coke, per cent Fuel ratio	68.63 1:1.98 McCreath.	71.375 1:2.27 McCreath.	81.00 T.T. Morrell.	71.00 T. T. Morrell.	83.59 1:4.78 McCreath.	85.24 1:5.30 McCreath.

## III. Non-coking Coals (Block Coal).

	Mercer County, Pa., Sharon Coal.		Mercer County, Pa.	Straitsville, Ohio.	Brazil, Ind.
Moisture Volatile matter Fixed carbon Sulphur	3.79 35.30 58.875 0.675 6.36	3.60 32.58 62.66 (0.85) 1.16	3.80 25.49 68.03 1.04 1.70	86.50 55.60 0.96 6.94	40.15 57.20 0.75 1.90
Total	100.000	100.00	100.06	100.00	100.00
Coke, per cent	60.91 McCreath.	Wormley.	Jno. Fulton.	61.00 Wormley.	58.00 Prof. Cox.

Effects of High or Low Temperature in the Distillation of Coal.—Coal when distilled at a low temperature yields products of a very different nature from those obtained if the temperature employed had been high. On this subject Professor Edmund T. Mills, of Glasgow, in his little manual on "Destructive Distillation" (3d ed., p. 9), states that "at a very high temperature the products from coal and shales are carbon and carbonized gases of low illuminating power, with but little liquid distillate; at a low temperature there is much liquid product and gas of high illuminating power. The greatest amount of liquid product of low boiling-point is found in American and Russian petroleums, which have probably been produced by the long-continued application of a very gentle natural heat.

"When coal is slowly heated (as must be to a great extent the case when it is broken fine, or when a large retort is used), its oxygen is chiefly converted into water; when rapidly heated, the oxygen is expelled as carbonic oxides."

To show the verification of these principles in practice, the results of high and low temperature distillation upon three different coals may be quoted from the same authority:

Yield of Gas, Oil, etc., from Shales and Coals at High and Low Heats.

	G000 S	SHALES.	Boghea	D COAL.	GAS COAL.			
	High heats. Low hea		High heats.	Low heats.	High heats.	Low heats.		
Gas. Ammonia-water Tar or oil Sulphur Water at 212°  Coke { Fixed carbon	13.65 3.65 11.04 0.99 2.82 32.15 4.16 1.05 62.64	2.54 6.47 17.65  26.66 10.81 62.58	37.82 2.43 20.65 0.18 0.80 61.38 9.01 0.06 29.55	4.88 3.28 50.29 58.85 12.40	20.49 3.09 17.08 0.29 4.15 45.10 45.00 0.34 9.56	6.49 7.24 26.45 		
	67.85 100.00	78,34 100.00	88.62 100.00	41.65	54,90 100.00	59.82 100.00		
Coke (dry) per ton of shale or coal Specific gravity of shale or coal	1,520 lbs.	1,642.2 lbs.	865 lbs.	934 lbs. 24	1,230 lbs.	1,340 lbs.		

Note.—The low heat results were gotten by distilling the sample in a two-inch iron tube in a gasfurnace.

Lunge (Coal-Tar and Ammonia, 2d ed., p. 17) states that "The quantity, and to a much greater extent the quality, of the tar are influenced by the temperature at which the decomposition of the case is carried on. Low temperatures, with nine thousand cubic feet of gas per ton of coal, will yield, with some coals, sixteen gallons of tar; whilst at high temperatures the yield will be but nine gallons, with about eleven thousand cubic feet of gas, from the same coal."\* If the temperature be a comparatively low one, mostly such hydrocarbons are formed as belong to a paraffin (methane) series, having the general formula  $C_nH_{2n+2}$ , along with the olefins,  $C_nH_{2n}$ . The lower members of this series are liquid, and, furnished in the pure state, are lighting and lubricating oils; the higher ones are solid and form commercial paraffin. They are always accompanied by oxygenized derivatives of the benzene series (phenols); but of these the more complicated ones predominate, in some of which methyl occurs in the benzene nucleus, in others replacing the hydrogen of hydroxyl,—e.g., cresol, CoII4(CH3)(OH); guaiacol,  $C_nH_4(OH)(OCH_3)$ ; creosol,  $C_0H_3(OH_3)(OH)(OCH_3)$ , etc. products prevail; and among the watery ones acetic acid (which is again a compound of the fatty series) is paramount. Of course also permanent gases are always given off, though in comparatively small quantity.

If, on the other hand, the coal has been decomposed at a very high temperature, the molecules are grouped quite differently. Whilst the olefins and members of the acetylene series still occur more or less, the hydrocarbons of the paraffin series disappear almost entirely; and from them are formed on the one hand compounds much richer in carbon, on the other hand more hydrogenized bodies. The latter always occur in the gaseous state; hence the gas so produced contains methane, or marsh-

<sup>\*</sup> Davis, Journ. Soc. Chem. Ind., 1886, p. 5.

DESTRUCTIVE DISTILLATION OF COAL.

gas, CH4, and free hydrogen as principal constituents, and is very much increased in quantity. The carbon thus set free is partly deposited in the retorts themselves, and then occurs in a very compact graphitoidal form; another portion of the free carbon occurs in a state of extremely fine division in the tar, and forms a constituent of the pitch or coke remaining behind from tar-distilling; another portion contributes to the formation of compounds richer in carbon, belonging to the "aromatic" series, all of which are derived from benzene, C<sub>6</sub>H<sub>6</sub>. At the same time the action of heat effects further molecular "condensations," usually with separation of hydrogen, by which process compounds of a higher molecular weight are formed, as naphthalene, anthracene, phenanthrene, chrysene, etc. The never absent oxygen must also in this case cause the formation of phenols; but here phenol proper, or carbolic acid  $C_6H_5(OH)$ , predominates, whilst cresol and the other homologues are diminished in quantity, and the dioxy-benzenes, as well as their methylated derivatives, disappear altogether. The above will be better illustrated by the statement (from Stohmann-Kerl's "Chemie," 3d ed., vi. p. 1162) that Zwickau glance coal yielded the following quite different products, according to whether it was put into a cold retort and gradually brought to a red heat (a), or distilled quickly from a very hot retort (b):

	a.	ь.
Coke	. 60.0	50.0
Water	. 10.7	7.7
Tar	. 12.0	10.0
Gas and loss	. 17.1	32.1

The tar from (a) consisted of photogen, paraffin oil, lubricating oil, paraffin, and creosote; that from (b), of benzene, toluene, naphthalene, anthracene (together with heavy oils corresponding to the paraffin and lubricating oil), and much creosote.

The annexed diagram, constructed by S. B. Boulton, and published in the Society of Chem. Ind. Journal, 1885, p. 471, represents the whole process of the destructive distillation of coal, including the subsequent treatment of the main fractions, and exhibits in their proper order the various products obtained therefrom.

#### II. Processes of Treatment.

1. Gas-retort Distillation of Coal.—The distillation of coal as carried out in retorts differs from distillations of other substances mainly in the apparatus employed and in the nature of the substances to be recovered. For gas purposes, retorts, wherein the decomposition of the coal used takes place, are made use of, which were originally constructed of cast iron, about one inch in thickness, twelve to fifteen inches in width, and about seven feet in length, closed at the rear end, and provided at the front or mouth with a heavy shoulder or rim supplied with study to which is attached a cast-iron extension, technically termed the "neck," which carries on its upper side a flange to which are secured upright pipes serving to lead the gases generated away from the retort.

The front of the neck is provided with a screw clamp to retain the lid or cap of the retort in position. Iron retorts are destroyed with great rapidity; the destruction being caused by the heat of combustion of the fuel used, the sulphur in the gas coal (an impurity always present in more or less quantity), which acts, forming sulphide of iron, and the carbon, which, as a carbide of iron, graphitic in appearance, forms layers within the retort from one to two inches in thickness. The oxygen of the air also has a very deleterious influence, especially upon retorts when heated to redness.

In later years fire-clay retorts have been substituted for those made of cast iron, for the reason that they are more durable. These retorts are made of a mixture of clay and sand, and are furnished to the gas-works in several shapes, the semi-cylindrical being the one most generally employed. The sizes vary, six to nine feet in length, fifteen to twenty inches in width, and from ten to fifteen inches in height being the average, and take a charge of one hundred and fifty to two hundred pounds of coal. Retorts have been made up to nineteen feet in length, being charged from both ends.

The retorts, varying in number from five to seven, or even nine and more, are mounted in brick furnaces of special construction, in such a manner that the gases of combustion of the coal will pass around and over the retorts and out through a main flue leading to the chimney. The fuel employed can be either coal, coke, or a mixture of both. Gas as a means of firing has been used for the purpose, the method being based upon the well-known regenerative system of Sir William Siemens.

The retorts are charged by hand, care being taken to evenly distribute the coal over the *sole*, or bottom, and to close it quickly. Various attempts have been made to perform this laborious work with mechanical means, but at present no entirely satisfactory substitute has been found.

The products of distillation pass from the retorts proper through the neck, and upward through cast-iron *stand-pipes*, which are provided with *goose-neck* outlets, dipping below the surface of water in what is termed the *hydraulic main*.

It is in this part of the process that the main bulk of the tar is obtained, together with the ammonia-liquor. The hydraulic main is provided with an overflow-pipe through which all the tarry matters pass, This overflow-pipe leads to the tar-well, wherein the liquid products collect.

The gas having been freed from the tarry matters, etc., contained, passes from the hydraulic main with a considerably elevated temperature, carrying in a vaporized state hydrocarbons that would separate as its temperature is lowered. It is necessarily very important to remove these volatile and condensable products, which is effected by causing the gas to pass through a series of pipes, which reduces its temperature very close to that of the atmosphere. The older form of condenser was a series of pipes completely covered with water, similar to the worms as at present employed in connection with spirit and other distillations. This arrangement was replaced, however, by the forms now universally

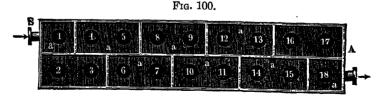
employed, and known as the atmospheric condensers, consisting of vertical pipes connected in pairs near the top by straight or curved pieces; the lower end of the upright pipes being connected to a box or trough containing water, divided by partitions, causing the gas to pass up and

down alternately, as shown in Figs. 99 and 100. Tarry matters and more ammoniacal liquor are again obtained, which find their way to the tar-well.

The gas after circulating through the condensers still contains impurities, which are removed by passing it through an apparatus known as the scrubber, consisting essentially of cylindrical wrought-iron towers filled with coke, over and through which trickles a light flow of water. or better, weak ammoniacal liquor; the gas passing upward meets this downward flow of liquid, and to it gives up the hydrogen sulphide contained, with the formation of ammonium sulphide. Tarry matters again are separated, and in time cause the coke to become somewhat clogged. This apparent drawback has led to the introduction of perforated iron plates in place of the coke, or, what has also proved equally efficient, wooden lattice screens. Anderson's rotating scrubber consists of brushes, which while rotating dip in a trough of ammoniacal liquor, and thereby perform functions similar to the means above mentioned. Another form of scrubber consists of a tower containing cast-iron plates provided with perforations, through which ammoniacal liquor passes in its downward course, meeting the gas. The liquid is continuously pumped to the top. when it again passes down, coming in contact with fresh gas. This is repeated until the liquor has



taken up sufficient ammonia to make it available to the ammonia sulphate manufacturer. From the scrubber the gas passes on to the purifiers, where the hydrogen sulphide still remaining, carbon-disulphide

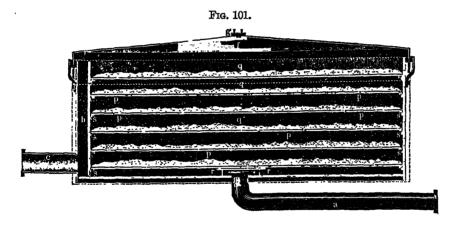


vapor, and the carbonic acid are removed. The purifiers ordinarily used consist of a large shallow box, constructed of cast iron in sections, and bolted together, or of wrought-iron plates, provided with a cover, the edge of which dips in water contained in a channel provided at the

top of the box, acting as a seal and preventing the escape of gas at that point, as shown in Fig. 101. The purifying agent first employed was slaked lime, which was spread upon wood screens, within the box, from four to six in number, one above the other, and supported by ledges. Hydrogen sulphide and carbon dioxide are absorbed by the lime, while compounds of cyanogen are at the same time decomposed.

Four purifiers are generally used, three being in service, while the fourth is reserved charged with fresh lime. Gas enters the one containing the oldest lime, and when it is noticed that lead-acetate paper is discolored by some of the gas acting upon it, it is known that the purifying material is saturated; this purifier is discontinued, and the freshly-charged one placed in service. In this manner they are continually rotated.

Ferric hydroxide (hydrated ferric oxide) is now largely employed in gas purification,—Laming process. Gas charged with hydrogen sulphide coming in contact with the above causes a reduction to ferrous sulphide,



at the same time some sulphur is deposited, with the formation of water. This process does not absorb the carbon dioxide from the gas; for this purpose lime is mixed with the ferric hydroxide, together with some cinders or sawdust, in order that the whole may be porous, and resist as little as possible the passage of the gas. When the purifying action has ceased, simply exposing the inert mixture to the action of the air for a while restores its properties, until after repeated use it becomes so charged with separated sulphur that it is no longer available.

The introduction of free oxygen into the gas, previous to it entering the purifiers, has been found to lengthen the time during which the oxide of iron can remain without being changed, thereby saving much handling. It has also improved the illuminating power of the gas. (Journ. Soc. Chem. Ind., vol. viii, pp. 84 and 694.)

From the purifiers the gas passes through the meter of the works, where the volume is registered, then on to the gas-holders, where it is stored and from which it is distributed.

The following	table	illustrates	the	composition	of	illuminating	ga
taken from various	s stag	es of manu	fact	ure:			

	Entering the air-con- denser.	Entering the scrubber.	Entering the Laming's purifier.	Entering the lime- purifier.	Entering the gas- holder.
Hydrogen Marsh-gas Carbonic oxide Heavy hydrocarbons Nitrogen Oxygen Carbon dioxide	87.97 89.78 7.21 4 19 4.81 0.81 8.72	37.97 38.81 7.15 4.66 4.99 0 47 3.87	37.97 38.48 7.11 4.46 6.89 0.15 8.39	37.97 40.29 3.93 4.66 7.86 0.48 8.83 0.36	87.97 89.87 8.97 4.29 9.99 0.61 0.41
Hydrogen sulphide	1.06 0.95	1.47 0.54	0.56		

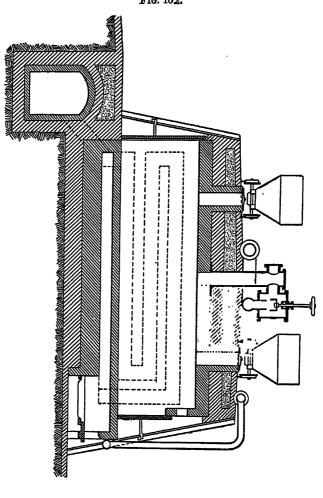
2. Coke-oven Distillation of Coal.—The burning of coke in pits "meilers," or mounds, represents the first rough and wasteful metho of converting bituminous coal into coke; involving, at the same time the total loss of all the volatile matter of the coal. It allows, however of the smothering the finished coke with fine dust, instead of requiring it to be quenched with water, as in other methods. The so-called "bee hive" ovens allow of the volatilizing of a much greater amount o sulphur in the coal, and give a decidedly increased yield of coke ove the pit-burning method. The charge can be run through, too, in less than half the time. Some air is admitted in both cases, with consequer loss of coke, and no attempt is made to save the residuals in either case.

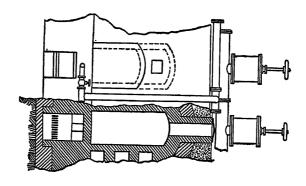
The distillation of coal in ovens differs materially from the olde methods of production in piles or kilns in that the inflammable gase given off are to some extent utilized.

Among the earlier forms of ovens planned for the collection of residuals (gas, tar, and ammonia) were the Appolt, which was a vertice oven surrounded by air spaces in which combustion took place, and the Coppée, which was a horizontal oven with vertical side canals for the combustion of gas and air. One of the most successful forms based upon the Coppée principle but using the Siemens regenerative firing is the Otto-Hoffmann oven, which has been extensively adopted in this country

The Simon-Carvés oven, illustrated in Fig. 102, on the other ham has horizontal heating chambers for gas combustion. Mr. Henry Simon C.E., in an address before the British Iron and Steel Institute (Jour Iron and Steel Inst., No. 1, 1880), states: "According to our system the coal is rapidly carbonized by subjecting a comparatively thin lay of it to a high temperature in a closed retort-like vessel, and, whilst is the bee-hive ovens the volatile products are burned inside, we burn the around and outside of this retort-like vessel, and only after they a deprived of the tar and ammoniacal liquor. Each oven is in the for of a long, high, narrow chamber of brick-work, and a number of the are built side by side, with partition-walls between them sufficient thick to contain horizontal flues. Flues are also formed under the flo







of each oven, and at one end of these is a small fireplace, consisting of fire-grate and ash-pit, with suitable door, the fire-door having fitte above it a nozzle, through which gas produced from the coking is ac mitted to form a flame over some fuel burning on the grate. Only very trifling amount of such fuel, consisting exclusively of the sma refuse coke, is used here, its function being really more that of ignitin the gas than that of giving off heat. These grates are not charged with fu more than twice in each twenty-four hours when in regular work. products of combustion pass from the fireplace along a flue under th oven floor to the end farthest from the fire. They return along anothe flue under the floor to the fire end: they then ascend by a flue in the partition-wall to the uppermost of several horizontal flues formed there in, and descend in a zig-zag direction along these flues, finall passing into a horizontal channel leading to a chimney. The oven i consequence is evenly heated at the bottom and sides, and the coal cor tained is rapidly and completely coked. No air enters the chambers, th only openings being for the escape of the volatile products. proved ovens are fed with coal by openings in the roof, over which coa trucks are run on rails; and the coal is evenly distributed by rakes intro duced at end openings, provided with doors faced with refractory mat rial, which doors are closed and kept tightly luted while the oven is i The feed-holes in the roof are also provided with cover Through the middle of the roof rises a gas-pipe provided with a h draulic valve, which closes the passage by a lip projecting down from into an annular cavity surrounding its seating, in which it is immerse in a quantity of tar and ammoniacal liquor, lodged there during previou The volatile products of the coal distillation rise by th gas-pipe, and are led through a range of pipes kept cool by extern wetting, so that the tar and ammoniacal liquor become condensed ar separated from the combustible gas." When the charge of coal has bee converted to coke, it is removed from the ovens by means of a pisto worked by an engine traversing rails in front of the battery. The yie of coke has been stated to be from seventy-five to seventy-seven per cer of the coal. During a run of two hundred and fifteen days, the vie of residuals averaged 27.70 gallons of ammoniacal liquors per ton coal carbonized, and 6.12 gallons of tar per ton of coal carbonized.

An improved form of oven analogous to the Simon-Carvés but wit improved utilization of heat and greater yield of residuals is the Seme Solvay, which has practically divided the field in this country with tl Otto-Hoffmann oven. While the regenerative heating is not used in tl Semet-Solvay oven, the air for combustion and sometimes the gas heated by the waste gases of combustion. It is claimed that by tl horizontal flue for the burning of the fuel gas a more uniform and high temperature is obtained.

Considerable difference exists between the tars obtained from t different coking processes above referred to. The Simon-Carvés t has a specific gravity of 1.106, and closely resembles, chemically, the ta produced in the illuminating (retort) gas process, both being obtain

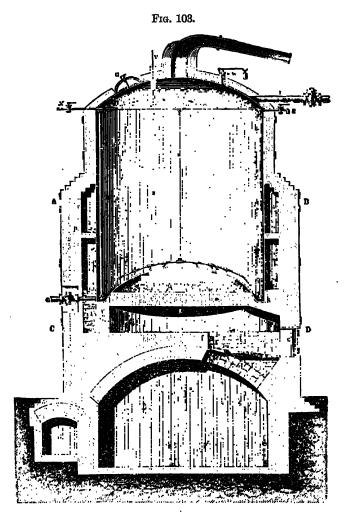
at a high temperature. The Simon-Carvés tar is rich in naphthaler and anthracene, but low in naphtha, benzene, phenols, etc. Analogo to this, as might be expected, is the Semet-Solvay tar. A sample fro Glassport, Pa., gave 3.7 per cent. light oils, 9.8 per cent. middle oil 12 per cent. heavy oils and 4.3 per cent. anthracene oil, and had specific gravity 1.170. On the other hand, a sample of Otto oven of (Lunge, Die Industrie des Steinkohlentheers und Ammoniaks, 4te Au: p. 87) gave light oil 3.4, creosote oil 14.5 per cent., crude naphthaler 6.7 per cent., and 27.3 per cent. anthracene oil. Much of the gas produced in the by-product coke oven contains benzol vapor and this washed out of it, so that much more is obtained than the percentage light oils in the tar would indicate.

The following comparison of Otto-Hoffmann coke oven tar with gretort tar from Dammer's Chemische Technologie der Neuzeit, vol. ip. 98, 1910) is instructive:

		Tar fro	m Otto-Ho oven.	offmann	Gas-tar.			
	Distillation temperature.	Dominion coal. Everett, Mass.	Dominion coal. Sidney, N. S.	Westphalian coal.	Germany.	Germany.	United States.	
Light oil	80°-170°C. 170°-230° 230°-270° Above 270°	1.26 14.76 7.07 21.38 53.03 1.52 1.01	1.38 11.46 8.56 20.63 53.68 1.93 2.36	6.55 10.54 7.62 44.35 30.55 trace 0.39	3.0 7.5 33.5 10.5 45.5	2.5 2.5 25.0 10.0 60.0	1.68 10.66 8.18 14.05 61.16 1.81 2.48	
Specific gravity		100.00 1.188	100.00 1.140	100.00 1.155	100.00 1.155	100.00 1.155	100.00	

3. Fractional Separation of Crude Coal-tar.—Following garetort distillation, in point of technical importance is certainly the distillation of the coal-tar obtained from the former processes and the separation therefrom of certain constituents which have a wide application is several industries. The same general mechanical arrangement, thoug somewhat simplified, is employed, consisting of a still, a condenser, an a receiver. The still should be constructed entirely of wrought iron and can be either horizontal or vertical. Horizontal stills are, according to Lunge, far less economical than the vertical. Fig. 103 is a vertical section of a tar-still showing the construction and fittings. The heat from the fire on the grate b is prevented from impinging agains the concave bottom of the still by means of the arch g, but passes throug the openings h in the circular wall k into vertical flues i, from whice it enters the annular space l and through flues in the front of the still to the upper space n, finally entering the flue p, which leads to the

chimney. The supply pipe r is for feeding the still, the pipe s is an overflow, and serves to indicate when the tank is full. The cock a is for drawing off the pitch. The still-head t is for conducting the vapors, and is connected with the condenser. The system of pipes x y z indicated is for conducting superheated steam into the still for finishing the distillation; the pipes conforming to the shape of the bottom, are pro-



vided with a number of jets for a more equal distribution of the steam. The remaining attachments require no further mention.

The condenser consists of a coil of pipe immersed in water contained in an iron tank. In England, the pipe used is from six to nine feet in length, and from four to six inches in diameter; the total length for one still is calculated at from one hundred and forty to two hundred feet. In Germany, preference is given to worms of iron (or lead, in which case

the pipe from the still must be continued below the surface of the water in the condenser and join the worm there, in order to obviate the possibility of it being melted), made of two-inch pipe, and mounted in eircular tanks provided with a steam-pipe for heating the water, and also with a small pipe connected with the worm for blowing in steam whenever it is necessary to clean it.

Connected with the condenser, and located at a safe distance from the still, is the receiver, which can be of any convenient shape, and of such a size as to contain the whole of one fraction; or a number can be employed, each acting as a store-tank and receiver. For the receivers to contain the volatile fractions, tight-closing covers must be supplied to guard against evaporation and fire, and the one containing the first fraction must have means for separating the oily from the watery layer. The receivers for the oils which deposit crystalline matter must be so arranged that they can be easily cleaned.

Coal-tar (Allen, Commercial Organic Analysis, 3d ed., vol. ii, Part ii, p. 47), "as obtained as a by-product in the manufacture of illuminating gas, is a black viscid fluid of a characteristic and disagreeable odor. The specific gravity ranges from 1.10 to 1.20, being usually between 1.12 and 1.15.

"As coal-tar is always more or less mixed with ammoniacal liquor, the consituents of the latter liquid are present in addition to those of the tar proper, and the constituents of the illuminating gas itself are also present in a state of solution.

"The first treatment of coal-tar on a large scale consists in distilling it in iron retorts and collecting the distillate in three or four fractions. The temperatures at which the receivers are charged vary considerably with the practice of different works, and hence the products are far from being strictly parallel."

The annexed table indicates the three most important methods of fractionation:

А.		В.		C.			
Product.	Distilling- point ° C.	Product.	Distilling- point ° C.	Product.	Distilling- point °C.		
Crude naphtha, or light oils. Heavy oils, dead oils, or creosote oils. Anthracene oils. Pitch	0 to 170 170 to 270 above 270	First runnings, or first light oils Second light oils Carbolic oils . Creosote oils . Anthracene oils Pitch	0 to 110 110 to 210 210 to 240 240 to 270 above 270	Light naphtha Light oils Carbolic oils . Creosote oils . Anthracene oils Pitch	0 to 110 110 to 170 170 to 225 225 to 270 270 to 860		

The principal constituents of coal-tar are separated, one from the other, by means of fractional distillation, a process depending upon the fact that, if a mixture of liquids, each having a different boiling-point, be heated, the one having the lowest will pass over first, and if the tem-

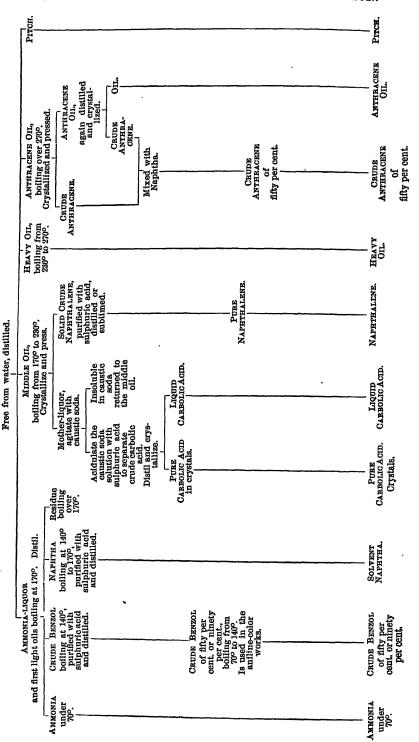
perature is not increased beyond that point at which the distillation this fraction takes place, no other constituent will come over; if the ter perature be gradually increased the others will follow in the order their boiling-points. In cases where the boiling-points are close, ar even in others where they are widely differing, the action of one su stance upon another often prevents exact separations.

The hot stills (from the previous working) are charged with free tar, all the openings are then closed, and the fire carefully watched order that no undue rise in temperature, and consequent boiling ov of the contents, may take place. Gases, ammonia-liquor, and light of distil over at 170°, the whole being designated "first runnings." Th fraction is collected and allowed to stand, when the watery portion se arates more or less completely from the oils, which are redistilled, viel ing ammonia boiling under 70°, crude benzol at 140°, which is subs quently purified with sulphuric acid and distilled, naphtha, 140° to 170 treated as the benzol, yielding "solvent naphtha." This whole fraction has a specific gravity nearly equal to that of water. The second fractic -"middle oil," or "carbolic oil"—distils over from 170° to 230°, ar contains the impure phenols or carbolic acid and naphthalene. It crystallized and pressed; the mother-liquor is agitated with caustic soc in an iron tank, the alkaline liquor (carbolate of soda) decomposed wi sulphuric acid, separating crude carbolic acid, which is distilled ar crystallized, yielding liquid and pure carbolic acid in crystals. unchanged oil from the soda treatment is returned to the second fractic for re-working. The press-cake from the first treatment of this fraction is purified with sulphuric acid, distilled, and yields naphthalene. third fraction constitutes the heavy or dead oil, so called from the fa that the specific gravity is greater than water, and boils from 230° 270°, occupying a position between middle oil and the anthracene fra tion. It is subjected to no further treatment, but is employed chief for preserving timber, varnish manufacture, burning for lamp-blac etc. The fourth fraction, or anthracene oil, boiling over 270°, constitut the green oil or green grease, from which, upon subsequent treatmer the commercial anthracene is obtained. This fraction is allowed to star for some time, in order to cool and to separate the crystallizable su stances, when the mass is drained from the excess of oil and presse The press-cake is crude anthracene, which is dissolved in naphtha ar known as fifty per cent. anthracene. The mother-liquor from the fir pressing and the drainings are redistilled, crystallized and presse yielding crude anthracene, treated as above, and anthracene oil. residue in the still constitutes pitch, which is withdrawn and employe for making pavements, varnish, etc.

The annexed diagram from Ost's "Lehrbuch der Technisch Chemie" graphically represents the preceding outline of the tar distill tion process.

4. TREATMENT OF AMMONIACAL LIQUOR.—The ammoniacal liquor the gas-works is that which passes out continuously from the scrubbe and other parts of the process, and is the chief source of nearly all the chief source of the process.

COAL-TAR,



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ammonia of commerce. According to Lunge, ordinary gas-liquor contains the following:

(a) Volatile at ordinary temperatures.Ammonium carbonates (mono-, sesqui-, and bi-).

Ammonium sulphide (NH<sub>4</sub>)<sub>2</sub>S.

Ammonium hydrosulphide, NH4.HS.

Ammonium cyanide.

Ammonium acetate (?).

Free ammonia.

(b) Fixed at ordinary temperatures.

Ammonium sulphate.

Ammonium sulphite.

Ammonium thiosulphate (hyposulphite).

Ammonium thiocarbonate.

Ammonium chloride.

Ammonium thiocyanate (sulphocyanide).

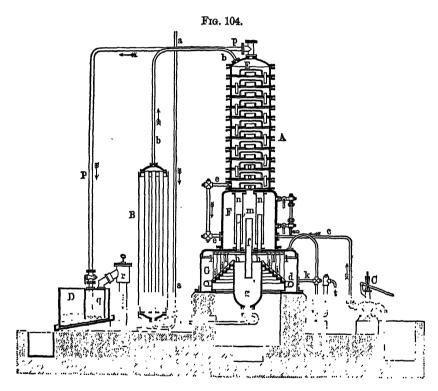
Ammonium ferrocyanide.

The salts of ammonia that are volatile are readily removed from the gas-liquor upon simply boiling, or by the aid of steam. The fixed ammonia salts require the addition of chemical agents—e.g., lime—to break up the combination and liberate the ammonia which is eventually recovered. The greater the amount of volatile ammonia and less the amount of the non-volatile compounds, the greater the value the liquor has for treatment.

The method of recovering ammonia at a London works, where one hundred thousand gallons of liquor are treated daily, is briefly outlined as follows: The liquor is pumped into a large settling-tank, where, after remaining for a day or more, it is pumped into a "Coffey" still, thirty feet high, into which steam at two atmospheres pressure is blown. By this treatment the volatile ammonium compounds are separated from the water and the non-volatile compounds. Carried along with the steam, the volatile compounds pass from the still through a worm, provided with half-inch holes, into a sheet-lead saturator filled two-thirds with 140° Twaddle sulphuric acid in water. This water so dilutes the acid that it prevents the ammonium sulphate from crystallizing within the saturator. After saturation, steam is blown through the solution to remove hydrogen sulphide, which, after passing through a condenser, is burned; the heat generated being partly utilized in the production of steam for the operation. The saturated liquid is run off into leaden pans placed over a fire, and evaporated to such a point that the sulphate will crystallize out. The residual mother-liquor is made use of in the dilution of the sulphuric acid in the saturator.

Without going into the details of construction of the many improvements made in the apparatus employed for the recovery of ammonia, it may be well to mention the apparatus of Grüneberg and Blum, Fig. 104. A is the column, B the economizer through which the gas-liquor passes before entering the still, and is heated by means of steam or waste gases.

C is the pump which introduces the lime into the lime-vessel F. D is the acid-tank or saturator. The gas-liquor enters the still at the top and descends from chamber to chamber, meeting the upward current of steam, till it reaches the lime-decomposition-tank F, and finally the boiler G. In this is a peculiar truncated cone, I, over which flows the liquor from step to step, and owing to the increased area of each step the liquor becomes thinner and thinner, permitting the steam to act very thoroughly. The ammonia generated passes from the still through the pipe P to the saturator D. Waste gases collect in the bell Q, from which they are led to the economizer B, and finally burned.



Feldmann's apparatus is a steam still, capable of recovering both the volatile and fixed ammonia, and occupies very little space. It consists of a chambered column, lime-tank, and an auxiliary column, in connection with feed-tanks, economizer, lime-pump, and saturator. The liquor flows from the feed-tanks through the economizer, where it is heated, to the top of the main column, down which it flows successively through the chambers in which it is boiled into the decomposing-tank, which contains lime, where it is thoroughly agitated with steam. The liquor flows from this tank to the auxiliary column, similar to the first one, where the little ammonia found is driven out. The spent liquor collects in the lower compartment, from which it constantly flows away. Lunge states that an apparatus to distil from eight to ten tons of ammoniacal

liquor daily occupies a space of seventeen feet by thirteen feet by te feet.

The sulphate of ammonia as it is fished from the saturators is allowed to drain, sometimes slightly washed with water, and sold without drying.

#### III. Products.

Under this head will be considered the more important products that are obtained by the subsequent treatment of the main fractions of the distillation process as indicated on previous pages.

1. First Light Oil is the fraction distilling at a temperature up to 170° C. It includes a small percentage of ammonia-liquor which is mechanically contained in the tar, and is separated from the tar oils by being allowed to stand and settle out, when it is drawn off. The specific gravity of the fraction is about .975, and is made up of benzene, toluene, and higher homologues, with phenol, cresol, naphthalene, etc. The products obtained from it are separated by redistilling the whole fraction in a small still of the same general type as the large tar-still. The separate distillates are generally as follows:

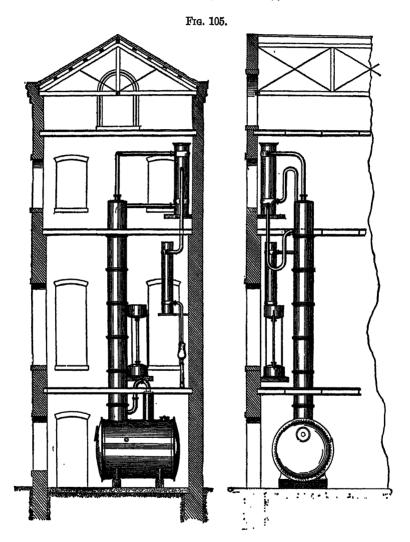
### First Light Oil up to 170° yields

(a)	To 110°		 	 	 	"90	per	cent.	benzol."
(b)	110° to 1	140°	 	 	 	"50	per	cent.	benzol."
	140° to								

The fraction obtained up to 110° is chemically washed, being agitated with sulphuric acid of 1.84 specific gravity in the proportion of one pound to one gallon of oil, which combines with the bases, dissolves resins, etc. The agitation is carried out in cast-iron or lead-lined wooden tanks securely covered to prevent loss of the volatile bodies, and provided with mechanical means for mixing. This is completed in ten or fifteen minutes, when the whole is allowed to stand at rest for an hour or more, and then the spent acid is completely removed. The oil is now thoroughly washed four or five times with water, until no color is imparted to the washings, which should have but a slight acid reaction. Agitation is again continued, but with a ten per cent. caustic soda solution, afterwards allowed to separate, when the alkaline solution is removed, and the oil is finally washed with water and distilled, either by means of fire or steam.

(a) "Ninety per Cent. Benzol."—The product coming over at 110° is designated "ninety per cent. benzol," from the fact that ninety per cent. by volume of it distils before the thermometer rises above 100° C. A. H. Allen (Commercial Organic Analysis, 2d ed., p. 489) states: "A good sample should not begin to distil under 80° C., and should not yield more than twenty to thirty per cent. at 85°, or much more than ninety per cent. at 100°. It should distil below 120°. . . . . The actual percentage composition of a ninety per cent. benzol of good quality is about seventy per cent. benzene, twenty-four per cent. toluene, including

a little xylene, and four to six per cent. of bisulphide of carbon and light hydrocarbons. The proportion of real benzene may fall as low as sixty or rise as high as seventy per cent. Ninety per cent. benzol should be free from opalescence and colorless ('water white'). The specific gravity is between .88 and .888 at 15.5° C. (=60° F.), but this is not a true



guide as to the quality, from the fact that bisulphide of carbon (specific gravity 1.27) and light hydrocarbons (specific gravity .86) sensibly affect the specific gravity of the benzol."

(b) "Fifty per Cent. Benzol" is a product of the fraction boiling from 110° C. up to 140° C., and is subjected to the same treatment as the previous one. The specific gravity of this benzol varies from .867 to .872 in the Scotch, to .878 to .88 in the English, samples. Is nearly

free from bisulphide of carbon, and contains little hydrocarbons, while the per cent. of toluene and xylene are greater than in the ninety per cent. benzol.

The "benzols" on the American market at present are: Benzol pure, boiling at 80°-83° C., and gravity .881 to .884; benzol one hundred per cent., gravity .875 to .884; benzol ninety per cent., gravity .875 to .882; benzol fifty per cent., gravity .871 to .875; benzol 160° (ninety per cent. at 160° C.), gravity .864 to .870; benzol straw color (crude, ninety per cent. benzol), gravity .862 to .870.

(c) Solvent Naphtha—so-called from the use to which it is put. dissolving caoutchouc in the manufacture of water-proof materials, etc., -follows the benzols, boiling over 140°, and consists of xylene, pseudocumene, and mesitylene. In some works the distillation of this fraction is not driven to the end, but stopped when the product yields ninety per cent. at 150° C., the residue being distilled as burning naphtha with a specific gravity of .90. Lunge states: "From the product distilled up to 140° may be extracted sixty or seventy per cent. of fifty per cent. benzol, twenty to twenty-five per cent. of carburetting and solvent naphtha, five to eight per cent. of burning naphtha. The product distilled between 140° and 170° yields twenty-five to fifty per cent. best naphtha, fifty to twenty-five per cent. burning naphtha, and twenty-five per cent. residue in the still." The separation of the preceding into benzene, toluene, xylene, etc., for the use of the color manufacturer. is not ordinarily carried out in the tar-distillery, but at the colorworks, in especially constructed column stills. The appearance of such a benzene rectification still is shown in Fig. 105. For details of construction of such a column still, see Chapter VI, p. 247.

The following table (Lunge, "Coal-Tar and Ammonia," 2d ed., p. 476) shows the yield in percentage volumes of the products from the light tar oils:

COMMERCIAL PRODUCTS.	Initial boiling points.	° C. 88.	98. 98.	° C. 100.	° C. 110.	° C. 120.	° C. 130.	° C. 188.	° C. 149.	° C. 160.	°C. 171.
"Ninety per cent. benzol" "Fifty per cent. benzol" Toluol Carburetting naphtha. Solvent naphtha. Burning naphtha.	° C. 82 88 100 108 110 138	30  	65 18 	90 54 	74 56 1	90 90 35 17	71 57	84 71	97 90 80	71.5	89

2. MIDDLE OIL.—This constitutes the second main fraction in the tar distillation process, and is collected between 170° and 230° C., yielding upon further treatment two very important and valuable products: liquid and solid carbolic acid and naphthalene, both of which find their widest application in the artificial-color industry, although large quantities are employed for many other purposes.

While this fraction is coming over from the still, no cold water is allowed to run into the condensing-tank, for the reason that a reduction

of temperature to the point at which solid naphthalene would form in the condenser is to be avoided; a steam-pipe is generally led into the tank, and the water brought to 50° or 60°, thereby keeping crystallizable matter in a fluid condition and continually flowing.

This distillate is allowed to become cold, when nearly all of the naphthalene separates in leaflets, which are drained and pressed to expel the remaining portions of the non-crystallizable oil, which is the source of the carbolic acid.

1. Carbolic Acid.—The above oils are thoroughly mixed with a solution of caustic soda (specific gravity 1.26) in a tank provided with mechanical agitators, or with means for forcing air through the liquids. The mixing is performed at a temperature of from 40° to 50°, and is completed in one to one and a half hours, when, after standing to allow the alkaline liquors to subside, they are drawn off and cautiously decomposed by adding sulphuric acid till the liquor has an acid reaction, when it is at once removed to avoid the crystals of sodium sulphate forming in the tank; the carbolic acid is allowed to stand for a few days in order that any sodium sulphate solution remaining may separate out, when it is washed with water and finally distilled in small retorts, yielding, in the first fraction, water and oil; in the second, crystallizable oil, from which is obtained the crystal carbolic acid of commerce; and in the third fraction, the non-crystallizable phenols, or liquid carbolic acid.

That part of the mother-liquor from the naphthalene which is not acted upon by the caustic soda solution added to remove the phenols is returned to the main middle-oil fraction and again re-worked.

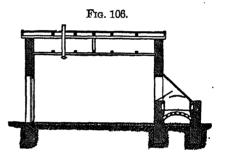
Carbolic Acid, or Phenol, CaHaO (or CaHaOH).—All compounds containing the group OH in place of one or more of the hydrogen atoms of benzene (C<sub>6</sub>H<sub>6</sub>) or its homologues, are designated Phenols. acid has a very peculiar and characteristic odor, burning taste, is poison. ous, and has preservative properties; the odor, however, is not so pronounced in pure as in impure specimens. The specific gravity at 0° is 1.084; it crystallizes in colorless rhombic needles which melt at 42°, boiling at 182°, and is not decomposed upon distillation. At ordinary temperature it dissolves in water with difficulty (1:15), but is soluble in alcohol, ether, glacial acetic acid, and glycerine in all proportions. Upon exposure to light and air it deliquesces, and acquires a pinkish color. most extensive use made of it is as a raw material in the manufacture of many of the artificial coloring matters,-picric acid, used as a yellow dye, and which finds considerable application in the manufacture of a number of high explosives. Large quantities of various qualities of carbolic acid are consumed annually for antiseptic purposes, both for domestic use and in surgery.

2. Naphthalene.—The crude crystals which were obtained when the middle-oil fraction was allowed to cool, and also from the treatment by distillation of the unchanged oil from the carbolic acid separation, are purified by fusing and mixing thoroughly with caustic alkali, if impure, followed by a washing with hot water, and afterwards with sulphuric acid; if the naphthalene operated upon is of a better quality, the alka-

line treatment may be dispensed with, and the refining commenced with the acid, which is of 1.453 specific gravity; Lunge states, however, that this is too weak, and recommends an acid of 1.70 specific gravity, 1.84 specific gravity being still better. The amount of acid used varies from five to ten per cent.; the mixing being performed in lead-lined tanks, after which it is washed with water several times, and to remove the remaining traces of acid weak caustic liquor is used. The naphthalene thus purified is sublimed in barrels hung over melting-pots suitably mounted, or in frame or brick chambers connected by proper openings with an iron melting-pan, the general construction of which is shown in Fig. 106. The best naphthalene is produced by distillation from stills, which are made shallow, with a very high dome. Larger quantities are handled by this method than by subliming.

Naphthalene, C<sub>10</sub>H<sub>8</sub>, is one of the principal constituents of coal-tar, occurring in it in various proportions from five to ten per cent.; it is also formed when the vapors of organic substances are passed through

tubes heated to redness. The specific gravity of naphthalene when solid is 1.158, at its melting point (79.2°) it is 0.978; it boils at 216.6° C. The odor is pleasant, though characteristic; volatilizes to some extent at ordinary temperature, but readily in the vapor of boiling water. Crystallizes in large, silvery-brilliant, thin rhombic plates, which are faintly soluble in hot, but insoluble in cold



water, though easily in methyl and ethyl alcohols, chloroform, ether, benzene, etc. The commercially sublimed naphthalene is from seventy to ninety-nine per cent. pure. Industrially, it is employed in the manufacture of a large series of coloring matters; as an enricher ("carburetter") of illuminating gas; and when specially refined, as a substitute for ordinary camphor in preventing the ravages of insects, etc., in woollen goods.

3. Creosote Oil, or Heavy Oil, constitutes the third main fraction, and is generally collected from 230° to 270° C., or until it is noticed that solid matters begin to crystallize, which indicates that the anthracene is commencing to distil. In order to prevent any cresols from contaminating the phenol and naphthalene of the previous fraction, that fraction is not driven to completeness, which precludes the possibility of any of the heavy oil passing over. Any naphthalene contained in this fraction is recovered by crystallizing and pressing, the residual oil not being subjected to further treatment but employed directly.

The oil has a greenish-yellow color, and is very fluorescent, which increases in intensity upon exposure to light and air. By transmitted light it is dark red, and by reflected light the appearance is bottle-green. The odor is unpleasant and extremely characteristic. It is heavier than water, the last portion coming from the still being as high in specific

gravity as 1.10. Creosote oil has been found to contain naphthalene, anthracene, phenanthrene, phenol, cresol, etc., with many other bodies but little known. It finds its widest application in the *creosoting* or *preservation of timber*; although, to a limited extent, it has been employed as a fuel, and for the production of illuminating gas, softening hard pitch, as a lubricant, for lamp-black production, etc.

The process of impregnating timber with coal-tar oils, with the view of preserving it against decay, dates from 1838, when a patent was granted to John Bethell. This process consists essentially of exhausting the already seasoned timber of air and moisture in a vacuum maintained by means of an air-pump; when the exhaustion is complete, the tar oil is allowed to enter the vessel, when it is at once absorbed by the pores of the wood. Various processes have been suggested from time to time, but those which have given the most complete satisfaction are nearly all based upon the one above mentioned. In the experimental work of the Forest Service of the U.S. Department of Agriculture on tie preservation a simpler and from many points of view a better process has been used in recent years. The ties are put into open tanks containing creosote oil, in which they are completely immersed, and the contents of the tank are gradually heated by closed coils carrying steam under pressure to a point at which moisture is eliminated as steam. After the lapse of sufficient time to allow the moisture and air from the pores of the wood to escape in this way, the hot ties are quickly transferred to tanks containing cold creosote oil, in which they remain until entirely cooled. In this way the oil is drawn into the pores of the wood as they contract and the wood fibre is not weakened by steaming and vacuum treatment.

Until recently in choosing a creosote oil for wood preservation most experts valued the tar acids and naphthalene as the important constituents, and demanded definite percentages of each. Now the weight of opinion is in favor of the heavy oils, which come over after naphthalene in the distillation, and considers the naphthalene as of small value. This is because naphthalene is volatile at all temperatures, and will entirely disappear from the wood in course of time. As an illustration of this may be quoted from Circular 141 of the Forest Service, U. S. Department of Agriculture, entitled "Wood Paving in the United States," the specifications of the City of Minneapolis for creosote oil for wooden block impregnation. These state "the specific gravity of the oil at 20° C. shall be at least 1.09; the oil shall be completely liquid at 25° C., and show no deposit on cooling to 22° C.; it shall not contain more than two per cent. of water nor more than three per cent. of matter insoluble in absolute alcohol or benzene; on distillation up to 150° C. nothing must come off, up to 170° C. two per cent., up to 210° from six to eight per cent., up to 235° from twenty to thirty per cent., up to 315° from forty to fifty per cent., up to 355° from sixty to eighty per cent." It will be seen that this calls for a relatively heavy oil containing high boiling fractions.

Prof. Gellert Alleman also, in discussing the results of the extrac-

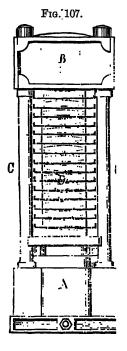
tion of oil from ties and paving blocks which had been in use for a term of years, says: "Perhaps the most striking thing is the disappear ance of the tar acids. It is certainly conservative to place the origina tar acid content at five per cent., yet the extracted oil showed but a tentl of this amount. . . . It appears therefore that light oils boiling below 205° C. will not remain in timber but that heavy oils containing a high percentage of anthracene oil will remain almost indefinitely and protect the wood from decay and boring animals. It is probable that naphthalene stays in wood for many years, but whether it is as valuable as anthracene oil is open to question. The value of the tar acids ha

apparently been overestimated by many persons, for although it has not been proved that they are valueless, they have been shown to possess poor

staying qualities."

4. Anthracene Oil.—The fraction distilling from 270° C. and over consists of that portion of the tar which is made up of bodies possessing the highest boiling points, and is distinguished from the heavy oil fraction by a separation, on cooling, of solid matters. In it have been found naphthalene, methyl-naphthalene, anthracene, phenanthrene, methyl-anthracene, pyrene, carbazol, etc. With the exception of methyl-naphthalene, which is a liquid, all the others are solids at ordinary temperature, but which have high melting points.

The separation of the crude anthracene from the distillate is accomplished by cooling or crystallizing, and pressing. The cooling takes place in large, shallow iron pans, either spontaneously or by refrigeration, when the semi-solid mass is transferred to bag filters, closed at the lower end, and connected by means of nipples at the upper end to a pipe for conducting compressed air, which acts in driving the liquid or non-solidi-

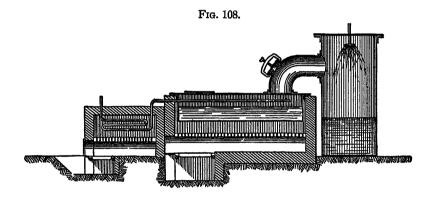


fying portion out, and leaving the mass nearly dry. By using filte presses instead of the above, a large and better yield can be obtaine in a shorter time. The crude anthracene is placed in cloths ar subjected to a gradually-increasing pressure in a vertical or horizont hydraulic press, the plates of which are so constructed as to be heate by steam, or the whole press may be enclosed in a chest to which stea can be admitted. Fig. 107 illustrates the general arrangement of press suited to the purpose. The use of heat in the pressing is to cau those bodies which have a lower melting point than that of the anthreene to be easily removed. The yield of anthracene by hot-pressing on comes up to about thirty to thirty-two per cent. of the oil in winte and thirty-three to thirty-six per cent. in summer (Lunge). The pressanthracene is ground to a fine powder, and washed with solvent naphtle (which removes the coal-tar oils) in either a horizontal or vertical at

tight boiler, fitted with a steam coil, and provided with a mechanical agitator. The mixing requires several hours with gentle heat, when the whole is forced by compressed air to a closed filter, which separates the now washed anthracene from the naphtha.

A still purer anthracene is obtained by submitting this product to sublimation with the aid of steam. For this purpose the apparatus shown in Fig. 108 is employed. The anthracene is melted in an iron pan, and over the surface of the melted mass superheated steam is blown. The anthracene vapors are carried by the steam into a cooling chamber, where they are condensed by coming in contact with a spray of cold water.

The anthracene oils from the first draining of crude material are usually re-distilled in order that the anthracene contained in them may be recovered. Graham's process (Chem. News, xxxiii, pp. 99, 168) for this is to distil about fifteen hundred gallons of the filtered oils from a



clean tar-still until crystals of anthracene are noticed, when a sample of the distillate is allowed to cool, at which point the operation is stopped, and the residue in the still is run out and allowed to become cold, when the product separates out. This is filtered and pressed in the manner above described for the first crystallization.

The oils which yield no more anthracene when subjected to further treatment are added to the creosote oils, or else employed to soften pitch, etc.

Anthracene, C<sub>14</sub>H<sub>10</sub>, is found under similar conditions to those giving rise to naphthalene, and was discovered in 1832 by Dumas and Laurent, while Fritzsche was the first to find it in coal-tar, in which it occurs as a characteristic constituent. When pure, it crystallizes in white, lustrous, rhombic plates, which exhibit a beautiful violet fluorescence. Melts from 210° to 213° C., subliming at about the same temperature in small scales. It is insoluble in water, sparingly in alcohol, while benzene, essential oils, light tar oils, and hot alcohol dissolve varying quantities. When oxidized it yields anthraquinone, which is further treated in the processes for the production of the valuable alizarine and other coal-tar colors, and which forms practically the only utilization for anthracene.

5. PITCH.—By pitch is understood the residue remaining in the sti after nearly all the volatile constituents have been driven off. For merly, what remained in the still after the light oils were distilled we called asphalt, and was equivalent to about eighty per cent. of the tax consequently it contained those constituents mentioned in the middle oil and creosote oil fractions, with the anthracene. This method of fractionation, however, is not followed, but the distillation is generally carried to that point when the distillate shows a specific gravity of 1.05 when soft pitch will result. If the distillation is carried further, or until it has a specific gravity of 1.12, hard pitch is obtained. In som cases the distillation is pushed as far as the still will stand with safety in which case no more volatile bodies remain and a coke virtually remains. As a rule, a moderately hard pitch is made, which is run interasks or barrels directly from the still.

The utilization of the pitch is carried out in several ways: in the manufacture of patent fuel (briquettes) when incorporated with coal dust or coke-refuse. This industry, which has had an extensive development in Europe, has in the last few years assumed importance in the United States. Briquettes contain from six to eight per cent. of pitch according to the amount of pressure employed in their manufacture.

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In deciding the value of a given pitch or tar for briquetting purpose three points may be noted: \* 1. The pitch or tar is distilled and a oils coming over below 270° C. are rejected as of no value for briqueting. 2. The flowing point of the portion to be used in briquetting determined. This should generally be not less than 70° C. 3. The pitc is extracted with carbon disulphide. The smaller the amount of residual carbon the more satisfactory the pitch.

# IV. Analytical Tests and Methods.

1. VALUATION OF TAR SAMPLES.—Practically, the most efficien method to follow for the determination of the value of tar samples to distil twenty or thirty gallons from a small still, in the same manne and under, as far as possible, the same conditions as is practised in th distillation of tar on a large scale. The products are weighed and mea When a small still is not accessible, recourse must be had, for laboratory purposes, to the following method, which gives excellent r sults if carefully attended: † "Two hundred and fifty cubic centimetre or ten ounces measure, of the tar is placed in a retort which it only on third fills, so as not to spoil the distillate if there is much frothing durir distillation. The retort should be supported on a cup-shaped piece coarse wire gauze, placed in an aperture in a sheet-iron plate. Over tl retort is placed a dome, made by removing the bottom from a tin can bottle, and cutting out a piece of the side to allow the neck of the reto to pass through. This contrivance confines the heat, and prevents t distillate or heavy vapor from falling back." . . . "The produc

<sup>\*</sup> U. S. Geological Survey, Bulletin 343, p. 41, 1908.

<sup>†</sup> A. H. Allen, Commercial Organic Analysis, 3d ed., vol. ii, Part ii, p. 52.

obtained by the distillation are: (1) Ammoniacal liquor; (2) total light oils; (3) creosote oil; (4) anthracene oils; and (5) pitch. In obtaining these fractions, the character of the distillate is amply sufficient to indicate the point at which the receiver should be changed. No thermometer is necessary, nor any condensing arrangement to be attached to the retort. The lamp being lighted (a powerful Bunsen), the ammoniacal liquor and naphtha are collected together in a graduated cylinder, which is changed when a drop of the distillate—collected in a test-tube of water—begins to sink. After standing to allow perfect separation of the ammoniacal liquor and light oils, the volume of each is observed, and, if desired, the strength of the former can be ascertained in the usual way by distillation with lime and titration of the distillate. The quantity of light oils is too small to allow of any further fractionation for benzols, etc.

"The next fraction of the distillate consists of creosote oil. At first it will contain much naphthalene, and will probably solidify in white crystals on cooling, but afterwards a more fluid distillate is obtained. At a still later stage, a drop of the distillate collected on a cold steel spatula will be found to deposit amorphous solid matter of a yellow or greenish-yellow color, when the receiver is again changed, the fraction measured, and if desired, assayed for carbolic acid and naphthalene.

"The next fraction of the distillate is rich in anthracene, and not unfrequently condenses in the neck of the retort as a yellow, waxy substance, which may be melted out by the local application of a small Bunsen flame.

"The collection of anthracene oil is complete when no more distillate can be obtained, and the pitch intumesces and gives off heavy yellow fumes. The distilled fraction is then measured and cooled thoroughly, and the resultant pasty mass pressed between folds of blotting-paper, weighed, and assayed for real anthracene by the anthraquinone test. The result is calculated into crude anthracene at thirty per cent., a standard which is generally adopted by the manufacturers.

"When the distillation for anthracene oil is complete, the retort may be allowed to cool, and when almost cold its body should be plunged into cold water. This produces a rapid surface-cooling and shrinking of the pitch from the glass, which may then be broken away and removed by gentle tapping, leaving the cake of pitch clean and ready for weighing."

2. Special Tests for Tar Constituents.—(a) Benzol.—The following method, from Allen,\* is the most convenient for testing benzol, and is reasonably accurate. One hundred cubic centimetres of the benzol to be tested is measured in an accurately graduated cylinder, and poured thence into a tubulated retort, of such a size as to be capable of retaining two hundred cubic centimetres, or eight fluidounces, when placed in the ordinary position for distillation. A delicate thermometer is fitted in the tubulure of the retort by a cork, so that it may be vertical and the lower end of the bulb be three-eighths of an inch distance from the bottom of the retort. The neck of the retort is then inserted into the

<sup>\*</sup> Commercial Organic Analysis, 3d ed., vol. ii Part ii n 185

inner tube of a Liebig's condenser, and pushed down as far as it will The condenser should be from fifteen to eighteen inches in length, and well supplied with cold water. The neck of the retort should not project too far into the condenser; if necessary it should be cut short. No cork or other connection is necessary between the retort-neck and condenser-tube. Before use, the tube of the condenser should be rinsed with a little of the sample, and allowed to drain, or some of the benzol may be sprayed through it. The graduated cylinder employed for measuring out the sample is next placed under the farther end of the condenser-tube in such a manner as to catch all the distillate, while allowing it to drop freely. The retort is then heated by the naked flame of a Bunsen burner (which can be conveniently placed in a tin basin containing sand or sawdust, in order to absorb the benzol in the event of the retort cracking). The flame should be small, about the size and shape of a filbert, and when the distillation of the benzol commences must be so regulated that the condensed liquid shall fall rapidly in distinct drops, not in a trickle or a continuous stream.

When the distillation commences the flame is regulated, if necessary, and the rise of the thermometer carefully watched. The moment it registers a temperature of 85° C. the flame is extinguished. Four or five minutes are allowed for the liquid in the condenser to drain into the measuring cylinder, and then the volume of the distillate is carefully read off and recorded. The lamp is then relighted and the distillation continued till the thermometer rises to 100° C., when the gas is turned off as before, and the volume of the distillate read off, after allowing time for drainage. The residual liquid in the retort is allowed to cool, and is then poured, to the last drop, into the measuring cylinder. A deficiency from the one hundred cubic centimetres originally taken will The difference between the collective volume generally be observed. after distillation and that of the original sample is to be added to the measure of the distillate collected at each temperature, and the corrected volumes reported as the "strength" of the benzol examined. a matter of fact, the loss of volume by distillation is due far more to expulsion of acetylene and other gases than to actual loss of benzol. Lunge, in "Coal-Tar and Ammonia" (2d edition, 1887), gives much practical information bearing upon this subject, which, in matters relating to the production and sale of benzols, etc., in Europe, has received considerable attention.

(b) Phenols.—The detection of phenol is in many cases of considererable importance, and several reactions have been proposed; the following are taken from Allen, who has personally verified them. Upon adding a drop of a dilute aqueous solution of phenol to a small quantity of a solution made up of one gramme of molybdic acid in ten cubic centimetres of sulphuric acid, a yellow-brown coloration is produced, which changes to a permanent purple tint. Many substances interfere with this reaction owing to the fact that it depends upon the reduction of the molybdic acid.

Ferric chloride gives a fine violet color, by which one part of phenol is detected in three thousand of water. Resorcin and hydroquinone give

similar reactions. Sodium chloride, nitre, or boric acid is unobjectionable, but most mineral and organic acids, acetates, borax, sodium phosphate, glycerine, alcohol, and ether hinder the reaction. If an aqueous solution of phenol is warmed with ammonic hydroxide and a solution of sodium hypochlorite, a permanent deep-blue color is obtained, which is turned red upon addition of acids. One part of phenol in five thousand of water will react if twenty cubic centimetres are used, weaker solutions also, after a time. A modification of the above is to add to fifty cubic centimetres of the phenol solution five cubic centimetres of dilute ammonia, and then, slowly, fresh and dilute bromine-water, when a fine blue tint is produced which is permanent. Bromine vapors will answer instead of bromine-water.

If to a solution of phenol a drop of aniline be added, and then a solution of sodium hypochlorite, yellow striæ are produced which change to blue. This test is very delicate.

Upon the gradual addition of bromine to a solution of phenol a white turbidity (mono-brom-phenol,  $C_0H_4$ BrOH) is formed. If the solution is dilute no precipitate occurs, but upon the addition of more bromine, di-brom-phenol ( $C_0H_3$ Br<sub>2</sub>OH) is formed; upon further addition of bromine a very bulky precipitate is produced, which is separated as the insoluble and characteristic tri-brom-phenol ( $C_0H_2$ Br<sub>3</sub>OH). This determination of phenol was first suggested by Landolt, though brought to perfection and used as a volumetric method by Koppeschaar (Z. a. Chemie, xvi, 233).

For the assay of carbolic acid the specific gravity is always noted, which ranges between 1.04 and 1.065; the lower figure indicates a suspicious sample, and represents light tar oils. Water is estimated by agitating the sample with half its volume of a saturated solution of salt, the loss of volume indicates the amount of water originally present. To ascertain the quality of crude carbolic acid and probable yield of crystallized phenol, the following method of Lowe (Allen, Com. Org. Anal., 3d ed., vol. ii, Part ii, p. 252) is used. One hundred cubic centimetres are distilled and the distillate collected in graduated tubes. Water first distils, and is followed by an oily fluid; this is allowed to stand, when the volume of water is read off. If the oily liquid floats on the water, it contains light oil of tar. It should be heavier than water, in which case it may be regarded as hydrated acid containing about fifty per cent. of real carbolic acid. The next portion of the distillate consists of anhydrous acid, and when it measures 62.5 per cent. the receiver is again changed. The residue in the retort consists wholly of cresylic acid and still higher homologues of carbolic acid. The 62.5 per cent. of anhydrous acid contains variable proportions of carbolic and cresylic These may be approximately determined by ascertaining the solidifying point, which should be between 15.5° and 24° C., and by making, with known proportions of carbolic and cresylic acids, a standard sample that will have the same solidifying point.

(c) Naphthalene.—The assay of this substance generally consists in submitting about twenty-five grammes, wrapped in several folds of

filter or bibulous paper, to pressure in a copying-press until the exud tion of any oil ceases, when the cake is again weighed, and if desirabl distilled from a small retort. Good samples should not distil below 210 and should yield ninety per cent. of distillate before the temperaturexceeds 225° C. Upon warming sublimed naphthalene with pure suphuric acid in a test-tube, the solution should remain colorless. If or per cent. of impurity is present, a decided pinkish tint is observe which is darker the greater the amount. The determination of the specific gravity, the melting point (79° C.), and the boiling point (216 to 218° C.) are made by the usual methods.

- (d) Creosote Oils.—The characteristics of this fraction were pr viously indicated. The specific gravity is determined either by the bottle or hydrometer; in cases where the sample contains much nap thalene, the specific gravity bottle is filled and the contents allowed become solid, when the stopper is worked in. A sample should become quite clear upon warming to about 38° C., and ought not become turb till cooled to 32° C. The liquefying point is determined by transfe ring a sample of the oil to a test-tube, immersing a thermometer, an warming gently till it becomes liquid. The point of turbidity is sim larly observed, by allowing the tube to cool spontaneously. For th determination of the naphthalene, one hundred grammes are chilled 4.5° C. in a small beaker, then transferred to a cloth filter, place in a funnel provided with means for cooling to 4.5° during filtration The filter and contents are removed and quickly pressed between bib lous paper in a copying-press, when the cake is pressed and weighed.
- (e) Anthracene.—Commercial anthracene contains a very variab percentage of real anthracene, the usual proportions being from thir to forty per cent., though formerly fifteen per cent. was common, ar special lots now assay over eighty per cent. The value of anthraced does not entirely depend upon the amount of real anthracene alor but also upon the freedom from objectionable impurities. In testing for paraffin, ten grammes of the sample are taken and treated with the hundred grammes of concentrated sulphuric acid, heated on a water bath for about ten minutes, or until the anthracene is dissolved, wheat may paraffin will rise to the surface in oily globules. The solution now poured cautiously into a tall beaker containing five hundred cut centimetres of water, stirred, and cooled, when the paraffin rises are solidifies on the surface; it is washed with water, dried between filter paper and weighed.

By the conversion of anthracene into anthraquinone the most satisfactory method of assaying is obtained. (See Allen, Com. Org. Ana 3d ed., vol. ii, Part ii, p. 230.) One gramme of the carefully sample specimen is placed in a flask holding five hundred cubic centimetre forty-five cubic centimetres of the very strongest glacial acetic acid added, and an inverted condenser, or long glass tube adapted to the flask. The liquid is then brought to the boiling point, and, while boing, the chromic acid solution is added to it gradually, drop by drop, I means of a tapped funnel passing through the india-rubber stopper

the flask, or inserted in the top of the vertical condenser. The chromic acid solution is prepared by dissolving fifteen grammes of crystallized chromic anhydride in ten cubic centimetres of water and ten of glacial The addition of the oxidizing agent should occupy two acetic acid. hours, and the contents of the flask should be kept in constant ebullition for two hours longer. The flask is then left for twelve hours, when the contents should be diluted with four hundred cubic centimetres of cold water, and allowed to rest for three hours longer. The precipitated anthraquinone is filtered off, and well washed on the filter with cold water, and with a boiling one per cent. solution of caustic soda and again with water. The anthraquinone is rinsed from the filter into a small dish, the water evaporated off, the residue dried at 100° C., and weighed. The following after-treatment is now universally employed: to the weighed residue ten times its weight of fuming sulphuric acid is added, and the whole heated to 100° C. on a water-bath for ten minutes, after which it is left in a damp place for twelve hours to absorb water, when two hundred cubic centimetres of water are added; the precipitated anthraquinone filtered off, washed with water, and then with one hundred cubic centimetres of a one per cent. boiling solution of caustic soda, and finally with boiling water, transferred to a dish, any water being evaporated off, and the whole dried at 100° C. and weighed. The weight of the anthraquinone multiplied by the factor. .856, gives the real anthracene in the weight of the sample.

Anthracene in Tar and Pitch.—Nicol (Z. a. Chemie, xiv, p. 318) treats twenty grammes in a small retort, receiving the vapors in a U tube kept at 200° C. The more volatile products do not condense, but the anthracene and other hydrocarbons do. When coking has taken place, the process is stopped, and the neck cut off, pounded, and the powder added to the distillate. The whole is then dissolved in glacial acetic acid and subjected to oxidation with chromic acid as above described. Watson Smith does not recommend the use of such a small quantity (twenty grammes); he employs a similar method but operates upon, at least, a litre, rejecting the portion distilling just before the coking. The anthracene oil is well mixed and an aliquot part employed.

- (f) Pitch.—The uses to which this residue is put are such that an elaborate method of valuation is unnecessary, although the method for asphalt is applicable. To distinguish between the two, one gramme of the sample is treated with five cubic centimetres of petroleum-spirit, and rapidly shaken. The mixture is filtered, and five to six drops of the filtrate diluted to five cubic centimetres with petroleum-spirit, when a greenish fluorescence will be noticed in the case of tar. Five cubic centimetres of rectified spirit should then be added, the mixture shaken and allowed to stand. The upper layer will consist of strongly-colored petroleum-spirit, while the lower layer of alcohol will have a golden-yellow color if coal-tar is present. In the case of mineral asphalt, the alcohol is faintly straw-yellow and often colorless.
- 3. VALUATION OF AMMONIA-LIQUOR.—Ordinarily, the Twaddle hydrometer is employed to determine the strength of ammonia-liquor; every degree of the instrument is taken to represent such an amount of

ammonia in the liquor so tested that one gallon will require two ounce of concentrated oil of vitriol to saturate it; by this means a liquor of 5 Tw. would be known as "Ten-ounce," 4° Tw. would be "Eight-ounce," etc. These results are fallacious, owing to the presence of substance which cause a false strength to be indicated.

The most accurate and practical method consists in decomposing tercubic centimetres of the gas-liquor to be assayed in a flask by means of solution of caustic soda, applying heat, and collecting the vapors of ammonia evolved in a known quantity of normal sulphuric acid contained in another flask suitably connected; the ammonia vapors neutralized part of this acid, and that which remains uncombined is exactly neutralized in the presence of litmus solution with normal ammonia, when the percentage of ammonia is at once determined.

4. Analysis of Illuminating Gas.—The analysis of illuminatin gas can be most conveniently carried out for technical purposes with th absorption apparatus devised by Hempel, although there are severe other forms in use which give results equally, and in some cases more accurate. Hempel employs, for measuring the gas under examination a cylindrical tube, similar to an ordinary burette, graduated to on hundred cubic centimetres in one-fifths, and mounted in an iron base This burette is open at the top, and at the bottom by means of a side tube. Another tube similar to the first, but without graduations, is use as a "level-tube," and is connected to the burette by a caoutchouc tub of sufficient length that the level-tube can be raised to the height of th former without inconvenience. There are also used pipettes, the ord nary form of which consists of two glass bulbs, connected by means c capillary tubes, and fastened to a board provided with openings t accommodate the bulbs, and mounted upon a foot. From one of th bulbs a siphon-shaped tube extends, which projects a short distance beyond the stand, and to which is attached a caoutchouc tube connec ing it with the top of the burette. The pipettes contain the sever liquids and solid reagents necessary to absorb the constituents of th Besides the simple form above mentioned, there is a "tubulate absorption pipette," so made as to allow the introduction of solids. an which can be readily altered to a pipette for the generation and reter tion of gases, as hydrogen and carbon dioxide, by means of zinc ( calcite respectively, the acid required for the liberation of the gas bein contained in the second bulb.

Another form is the "compound absorption pipette," which is en ployed for containing the reagents readily decomposed upon exposur to the atmosphere, or which give off noxious vapors.

The method of operating is as follows: The level-tube, previous filled with water, is raised until the gas-burette is completely filled, whe it is connected by means of a caoutchouc tube to the "aspirating-tube, or source of the gas, when the level-tube is lowered, and the water flow out, causing the gas to take its place in the burette; one hundred cub centimetres are obtained, which is noticed by causing the water-level each tube to coincide with the 100-cubic-centimetre mark on the low end of the burette. The absorption of the several constituents tak

place on connecting the top of the burette to the end of the siphonshaped tube before mentioned, when the level-tube is raised, and the gas is forced from the burette into the bulb of the pipette, the absorbent in which has been forced into the second bulb. When all the gas has passed over, compressors are applied and the pipette detached, and very gently agitated from two to five minutes, in which time the absorption will be complete; the pipette is again attached, the level-tube lowered, when the remainder of the gas is drawn back to the burette, which is closed, the water-level in each brought to coincide, and the reading taken. The difference between this reading and the original volume of gas taken is the volume absorbed. One constituent after another is in this way withdrawn by using pipettes containing solutions having affinity for the several gas components, as indicated below:

Carbon dioxide (CO2). Ethylene  $(C_2H_4)$ . Propylene (CaHa). Butylene (C,H8).

Benzene vapor (CoHs).

Oxygen (O).

Carbon monoxide (CO).

Hydrogen (H). Methane (CH4). Nitrogen (N).

Solution of potassium hydroxide.

Fuming sulphuric acid or bromine-water. After agitation, the vapors remaining in the gas are removed by contact with potassium hydroxide solution.

Fuming nitric acid may be employed, and the nitrous vapor remaining removed by agitation in the potassium hydroxide pipette, or absolute alcohol is used.

An alkaline solution of pyrogallol, or phosphorus chips in the presence of water, can be used.

A solution of cuprous chloride in hydrochloric acid or ammonia.

Residue, uabsorbed. Constituents determined by combustion, mixing the residual gas with air, and passing the mixture over palladium sponge.

# V. Bibliography and Statistics.

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#### STATISTICS.

#### 1. WOOD DISTILLATION IN THE UNITED STATES.—

				Hard woods.	Soft woods.	Total.
1907.	Cords	of	wood	distilled1,219,771	62,349	1,282,120
1908.	Cords	of	wood	distilled 878,632	99,212	977,844
1909.	Cords	of	wood	distilled1,149,847	115,310	1,265,157
1910.	Cords	of	wood	distilled1,257,997	192,442	1,450,439

Of the 147 plants in operation in 1910, 117 were engaged in the distillation of hard woods, and 30 in the distillation of soft woods.

2. Production of Coke in the United States (in Tons of 200 Pounds).—

	1909.	1910.
Total production	35,076,902	36,228,773
Valued at\$	31,638,058	\$82,714,095
Of which Pennsylvania produced	23,098,483	22,875,000
Valued at\$	46,196,966	\$45,978,750

3. Production of Coke, etc., in By-product Ovens (in Tons of 200 Pounds).—

	1909.	1910.
Number of by-product ovens	3,914	4,078
Coke produced in tons	6,254,644	7,138,734
Value of coke produced\$	21,703,462	\$24,793,016
Value of by-products		8,479,517

## These by-products in 1910 consisted of:—

27,692,858 cubic feet of surplus gas, valued at\$3,01	7,908
66,303,214 gallons of tar, valued at	
70,247,543 pounds of sulphate of ammonia, valued at 1,84	1,062
20,229,421 pounds of anhydrous ammonia, valued at 1,72	5,266
4,654,282 gallons of ammoniacal liquor, valued at 29	
Total	9,557

England produces the largest quantity of coal tar of any country: the world, the production in 1901 having been 908,000 tons.\* The tot world's production has been estimated at 3,000,000 tons.

<sup>\*</sup>G. Müller, Die chem. Industrie, Leipzig, 1909, p. 334.

- G. Lunge,\* from information gathered by himself, puts the production of coal-tar for 1886 in Holland at 20,000 to 22,000 tons, in Belgium at about 30,000 tons, and in the United States at 120,000 tons, of which some 60,000 tons are distilled, 37,000 tons are employed for manufacturing roofing-paper, roof-coating, etc., and some 23,000 tons are used up in the raw state.
- 4. OF COAL-TAR DISTILLATION PRODUCTS.—The estimate of Mr. Wilton of the coal-tar production of the United Kingdom for 1885, which was 643,000 tons, includes the following additional details:

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Ammoniacal liquor from tar alone.. 3,600,000 gallons = 1200 tons of sulphate.
Carbolic acid (crude) ...... 600,000
Of this, there was liquid creosote. 10,800,000
 Of this, there were creosote salts
   (crude naphthalene, etc.)....
                          56,620 tons.
 Corresponding to pure naphtha-
                          25,620 "
   lene .....
Benzol and toluol ...... 1,500,000
                         620,000
Solvent naphtha .....
                           3,420 tons.
Anthracene (pure) .....
                         396,000 "
Pitch .....
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5. PRODUCTION OF SULPHATE OF AMMONIA.—a. World's Sulphate of Ammonia Production. (In metric tons of 2204.6 pounds.)

1905.	1906.	1907.	1908.	1909.	1910.
England273,550	294,170	318,400	330,450	354,747	374,925
Germany190,000	235,000	287,000	313,000	330,000	373,000
United States 59,250	68,000	90,120	79,500	96,600	105,143
France 47,300	49,100	52,700	52,600	53,600	56,000
Belgium and Holland 24,200	30,000	55,000	35,000	40,000	43,000
Spain 10,000	10,000	12,000		12,000	9,000
Italy 4,500	5,000	11,000	80,000	12,000	12,000
Other countries 40,500	40,000	65,000		73,000	79,000
<del></del>					
694,300	731,270	891,200	890,550	971,947	1,052,068

b. Ammonium Sulphate and Sulphate Equivalent Produced in the United Kingdom. (In tons of 2240 pounds.)

1905.	1906.	1907.	1908.	1909.	1910.
Gas works155,957	107,160	165,474	165,218	164,276	167,820
Iron works 20,376	21,284	21,024	18,131	20,228	20,139
Shale works 46,344	48,534	51,338	53,628	57,048	59,113
Coke ovens 30,732	43,677	53,572	64,227	82,886	92,655
Producer gas and			•	-	•
carbonizingworks 15,705	18,736	21.873	24.024	24,705	27.850

c. United States Ammonia Production, Expressed in Sulphate Equivalent. (In tons of 2000 pounds.)

1905	 65,296	1908	83,400
1906	 75,000	1909	106,500
1907	 99,309	1910	116,000

<sup>\*</sup> Lunge, Coal-Tar and Ammonia, 2d ed., p. 15.

## CHAPTER XII.

#### THE ARTIFICIAL COLORING MATTERS.

# I. Raw Materials.

1. Hydrocarbons.—Benzene Series.—In the manufacture of the arricial coloring matters, the hydrocarbons which find application as ramaterials are limited mainly to benzene, naphthalene, and anthracen their homologues and derivatives; of which, probably, benzene is the most important.

The benezene series is as follows:

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		Boiling-point.	Specific gra	vity.	
Benzene, CoHo		. 80.4° C.	.884 at	15°	t
			.869 at	15°	ſ
	o-Xylene	142° C.	.893 at	0°	í
Xylene, CoH4. (CH3)3	o-Xylene	. 139° C.	.881 at	0°	(
	p-Xylene	138° C.	.880 at	0°	1
Pseudocumene,	(CTT )	169.5° C.	.895 at	0σ	(
Mesitylene, \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \	.(CH <sub>3</sub> ) <sub>3</sub>	( 165° C.	.865 at	14°	1
Durene, C6H2. (CH3)4.	(Fuses at 79°-80° C.)	. 192° C.			
Pentamethylbenzene,	$C_6H.(CH_3)_5$ . (Fuses at 5.5° C.).	. 231° C.			
Hexamethylbenzene, C	$C_6(CH_8)_6$ (Fuses at 166° C.)	. 265° C.			

Of which only the first three are employed to any extent.

Benzene has been described in a previous chapter (see Tar Distillation), but for the manufacture of colors an explanation is necessary the name benzene, chemically speaking, does not refer to the light frations obtained from petroleum, but applies solely to the substance ditilled from coal-tar; boiling at 80.4° to 81° C., having a specific gravit of 899° at 0°, with the definite composition  $C_6H_6$ . The term benzol, c the other hand, is not given to a definite compound, but to a mixture c benzene with variable quantities of toluene and xylene, with the other homologous of the same series. The quantity of these homologous bodicontained has an influence upon the use to which the aniline oil obtaine (by subsequent treatment of the benzol) can be put.

The pure benzene, free from the high-boiling homologues, is succe sively converted through several processes to dimethylaniline, which the base of the valuable methyl-violets. For the fuchsine process, berzol, seventy-five per cent. of which distils between 80° and 100° C. (containing toluene), is employed, producing aniline, seventy-five per cent of which distils between 180° and 190° C. High-boiling benzol, 115° 120° C., yields aniline, which is the starting-point for the production of the beautiful series of xylidine scarlets; the introduction, however, opure xylene has served to displace the above. Allen states (Commerci Organic Analysis, 2d ed., vol. ii, p. 489), "Ninety per cent. benzol is

product of which ninety per cent. by volume distils before the thermometer rises above 100° C. A good sample should not begin to distil under 80° C., and should not yield more than twenty to thirty per cent. at 85°, or much more than ninety per cent. at 100° C. It should wholly distil below 120° C. An excessive distillate—e.g., thirty-five to forty per cent. at 85° C.—indicates a larger proportion of carbon disulphide or light hydrocarbons than is desirable.

"The actual percentage composition of a ninety per cent. benzol of good quality is about seventy of benzene, twenty-four of toluene, including a little xylene, and four to six of carbon disulphide and light hydrocarbons. The proportion of real benzene may fall as low as sixty or rise as high as seventy-five per cent. Ninety per cent. benzol should be colorless and free from opalescence."

"Fifty per cent. benzol, often called 50/90 benzol, is a product of which fifty per cent. by volume distils over at a temperature not exceeding 100° C., and forty per cent. more below 120°. It should wholly distil below 130°."

"Thirty per cent. benzol is a product of which thirty per cent. distils below 100°, about sixty per cent. more passing over between 100° and 120°. It consists chiefly of toluene and xylene, with small proportions of benzene, cumene, etc."

The following table from Schultz (Steinkohlentheers) indicates the general properties of the three commercial benzols above described when subjected to distillation:

																								Thirty per cent.	Fifty per cent.	Ninety per cent.
To "	85° 90° 95° 100°							•			•	•		:	•				•	•		:	- :	0 2 12 30	0 4 26 50	25 70 83 90
"	105° 110° 115° 120°	•	•	:	•	:	:	:	•	:	•	:	•	:	:	:	•	:	•	•	•	•	•	42 70 82 90	62 71 82 90	94 97 98 99

The theoretical quantities of commercially applicable products from benzol are:

```
For 100 parts, 157.6 parts nitrobenzol.
"""" 119.2 "aniline.
"""" 215.3 "dinitrobenzol.
"""" 155.1 "dimethylaniline.
""" 191.0 "diethylaniline.
```

Toluene, or Methylbenzene, C<sub>6</sub>H<sub>5</sub>.CH<sub>3</sub>, is obtained by careful distillation of coal-tar benzols, and can be obtained from the balsam of tolu and other sources. It is quite similar in its properties to benzene; fluid at ordinary temperatures, and when pure boils between 110° and 111° C. Specific gravity .869. It is employed for the production of

nitrotoluene, toluidine, benzylchloride, benzalchloride, and benzald hyde,—the base of a valuable series of green colors. The theoretic yield of commercial products from toluene is as follows:

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For 100 parts, 148.9 parts nitrotoluene.
""" 116.3" toluidine
""" 115.3" benzaldehyde.
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Xylene, or Dimethylbenzene, C<sub>6</sub>H<sub>4</sub>.(CH<sub>3</sub>)<sub>2</sub>, exists under similar conditions to toluene, and is found in coal-tar. There are three xylene the ortho-, meta-, and para-, the second being most abundantly obtaine Owing to the slight difference between their respective boiling-point a commercial separation by distillation is practically impossible.

The annexed table gives the nature and behavior of the three is meric hydrocarbons mentioned.

	Ortho-xylene.	Meta-xylene.	Para-xylene.
Melting point Boiling-point Specific gravity  Dilute nitric acid  Permanganate Chromic acid . Sulphuric acid (66° Bé.) Sulphuric acid (fuming) Melting point of the sulphochloride Melting point of the sulphamide	o-Toluic acid, melting point 102° C. Phthalic acid. Decomposed. Sulphonic acid. Sulphonic acid.	Fluid. 189° C8668 at 19° C. m-Toluic acid, melting point 160° C.  } Isophthalic acid. Two sulphonic acids. Two sulphonic acids. (a) 34° C., (b) liquid. (a) 187° C., (b) 96° C.	15° C. 187.5° to 188° C8621 at 19.5° C. p-Toluic acid, melting point 178° C. Terephthalic acid No change. Sulphonic acid. 26° C. 148° C.

From Schultz, "Steinkohlentheers."

Naphthalene Series.—Naphthalene, C<sub>10</sub>H<sub>8</sub>, as a raw material, enter largely into the production of the extensive series of azo-coloring maters, and for such use it is converted into intermediary products, c which the alpha- and beta-naphthols are the most familiar. The occur rence, properties, and production of naphthalene are referred to o page 419.

Methyl-naphthalene,  $C_{10}H_7CH_3$ .—Two isomers exist in coal-tar, an can be separated from that fraction of the distillate boiling at from 220° to 270° C. The first of these is a liquid boiling at 243° C.; specifigravity 1.0287 at 11.5°. The second is a solid, looking like naphthalene melting at 32.5° C. and boiling at 242° C.

Ethyl-naphthalene,  $C_{12}H_{12}$ .—Two isomers,  $\alpha$ - and  $\beta$ -, are known  $\alpha$ -Ethyl-naphthalene, produced from  $\alpha$ -brom-naphthalene and ethy bromide, and distilled in vacuum, boils at from 257° to 259.5° ( $\beta$ -Ethyl-naphthalene, from  $\beta$ -brom-naphthalene, ethyl bromide, an sodium, boils at from 250° to 251° C.

Diphenyl,  $C_{12}H_{10}$ , has been found in coal-tar, and is readily obtaine when benzene vapors are passed through a red-hot tube. It is insolubly

in water, soluble in hot alcohol and in ether. It forms large colorless scales, melting at 71° C. and boiling at 254° C. Oxidized by chromic acid, it yields benzoic acid.

Stilbene,  $C_{14}H_{12}$ .—This compound, which is diphenylethylene ( $C_6H_5$ .CH = CH.C $_6H_5$ ), is formed when toluene or dibenzyl is led over heated lead oxide. It crystallizes in colorless scales, melting at 125° C. Forms the basis of numerous important dyes.

Anthracene Series.—Anthracene,  $C_{14}H_{10}$ , reference to which has been made in the previous chapter, is employed for the production of alizarine and allied bodies, the successful introduction of which caused a revolution in the processes of dyeing, and made useless for the time great areas of land which were devoted to the culture of madder. Anthracene, as it occurs in commerce, is rarely pure, being made up of a very large number of hydrocarbons, several of which have not been investigated. The following may be mentioned:

Methyl-anthracene,  $C_{15}H_{12}$ , closely resembles anthracene. It differs from that body in having a methyl group substituted for an H atom of one of the benzene rings. It occurs in coal-tar in small quantity, and owing to the high boiling-point, over 360° C., it is found in the anthracene. Crystallizes in pale-yellow leaflets, melting at 199° to 200°.

Phenyl-anthracene,  $C_{20}H_{14}$ , is formed when phenyl-anthranol or corrulein is heated with zinc-dust. Slightly soluble in hot alcohol, ether, benzene, carbon disulphide, and chloroform, and, upon cooling, crystallizes from the above solvents in yellow plates, melting at 152° to 153° C. The solutions have a blue fluorescence.

Fluorene, or Diphenylen-methane, C<sub>13</sub>H<sub>10</sub>, is found in coal-tar, and can be obtained by passing diphenylmethane through a combustion-tube heated to redness; it can also be obtained by distilling diphenyleneketone over heated zinc-dust, or by heating the same substance with hydriodic acid and phosphorus from 150° to 160°. Very soluble in hot alcohol, less in cold; crystallizes in colorless plates having a violet fluorescence. Melts at 113° C., boils at 295° C.

Phenanthrene, C<sub>14</sub>H<sub>10</sub>.—This hydrocarbon is isomeric with anthracene, is found with it, and forms a large part of, the last fraction of coal-tar. Compared with anthracene, the melting point is considerably lower, while the boiling-points are somewhat closer. It is much more soluble in alcohol, by which means a separation is effected; the low melting point materially assisting. Crystallizes in colorless, shining plates, melting at 100° and boiling at 340°, insoluble in water, but soluble in fifty parts of alcohol in the cold, and in ten parts on boiling; easily soluble in ether and benzene. It imparts a blue fluorescence when dissolved. When oxidized, phenanthrenquinone is formed. Technically, but little use is made of it, being chiefly employed in the oil baths for alkali melts, heating autoclaves, subliming phthalic anhydride, etc.

Fluoranthene, C<sub>15</sub>H<sub>10</sub>, occurs in the highest boiling tar fractions; crystallizes in needles; melts at 109°.

Pseudophenanthrene, C<sub>16</sub>H<sub>12</sub>, is found in crude anthracene, and crystallizes in large glistening plates, which melt at 115°. Pyrene, C<sub>16</sub>H<sub>10</sub>,

Retene, C<sub>18</sub>H<sub>18</sub>, Chrysene, C<sub>18</sub>H<sub>12</sub>, and Picene, C<sub>22</sub>H<sub>14</sub>, are bodies whi occur in the highest fractions with fluoranthene, and cannot be classe as raw materials,—no technical importance being attached to them.

2. Halogen Derivatives.—From Benzene.—The following table the halogen derivatives of benzene indicates those whose constitution known. They are produced by the action of the halogens upon the hydrocarbons directly, or through the action of the halogen compound of phosphorus upon phenols and aromatic alcohols. Two classes as produced, substitution and addition compounds. The former occurnder ordinary conditions, while the latter are formed when the reaction takes place in direct sunlight. Of the two, the substitution products as the more stable, the addition products being easily decomposed.

The following table gives the formulas of the several halogen derivatives of benzene and the boiling-points of the more important of the several isomeric compounds:

			Halog	en subst	titution	products	of ben	zene.			
C <sub>6</sub> H <sub>6</sub> C <sub>6</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> C <sub>6</sub> H <sub>8</sub> C <sub>6</sub> H <sub>2</sub> C <sub>6</sub> H C <sub>6</sub>	Cl Cl <sub>2</sub> Cl <sub>3</sub> Cl <sub>4</sub> Cl <sub>5</sub> Cl <sub>6</sub>	188° 179° 218° 246° 276° 882°	172° 208° 246°	178° 218° 254°	$\begin{array}{c c} Br \\ Br_2 \\ Br_3 \\ Br_4 \\ Br_5 \\ Br_6 \end{array}$	154° 224° 276° 329°	219° 278°	219°	I I <sub>2</sub> I <sub>3</sub> I <sub>4</sub> I <sub>6</sub>	185° 277°	285°

From Toluene.—(1) Benzyl-chloride (Chlorbenzyl),  $C_0H_5CH_2.Cl$  results from the action of hydrochloric acid upon benzyl alcoho ( $C_0H_5.CH_2.OH$ ), or by acting on boiling toluene with chlorine, thi method being the one most generally used; the product is washed with water containing a little alkali, when it is freed from impurities by distillation. It is a colorless fluid, specific gravity 1.113, boils at 179° insoluble in water, but soluble in alcohol and ether, and possesses ar exceedingly penetrating odor, acting upon the eyes and mucous mem brane of the nose. Technically, it finds considerable application in the color industry.

- (2) Benzal-chloride, C<sub>6</sub>H<sub>5</sub>.CH.Cl<sub>2</sub>.—Formed when chlorine acts upon boiling benzyl-chloride, or when phosphorus penta-chloride acts upon benzaldehyde. It is a colorless liquid, having ordinarily but little odor, but upon the application of heat gives off a vapor producing effects similar to the preceding. Boils at 206° to 207°; specific gravity at 16° 1.295.
- (3) Benzo-trichloride, C<sub>0</sub>H<sub>5</sub>.C.Cl<sub>3</sub>, is obtained by acting with chlorine upon boiling toluene until no further increase in weight takes place when it is washed in water containing alkali, dried, and distilled in ε vacuum. Boils at 213° to 214°; specific gravity 1.38 at 14°. It has a penetrating odor, and is highly refractive.

Bromine Derivatives of Xylene.—These are obtained when bromine is allowed to act upon the hydrocarbon or its isomers, or upon bromi-

nated compounds of the same, with or without the presence of iodine. They find no application industrially.

Halogen Derivatives of Naphthalene.—(1) Naphthalene Dichloride, C<sub>10</sub>H<sub>8</sub>Cl<sub>2</sub>, is a liquid, easily decomposed; produced as an addition com-

pound by the action of chlorine gas upon naphthalene.

- (2) Naphthalene Tetrachloride, C<sub>10</sub>H<sub>8</sub>Cl<sub>4</sub>.—This substance is manufactured in large quantities by passing chlorine gas through the melted hydrocarbon in a suitable apparatus, or by grinding the naphthalene to a paste with water and intimately kneading therein sodium or potassium chlorate, moulding into balls, and drying, after which they are immersed in concentrated hydrochloric acid. It crystallizes from chloroform in large rhombohedra, melting at 182°, and when boiled with nitric acid is converted into phthalic acid, which is the chief product obtained from it.
- (3) a-Brom-naphthalene, C<sub>10</sub>H<sub>7</sub>.Br.—Formed by the direct bromination of the hydrocarbon, or by the substitution of bromine for the amido group in a brom-a-naphthylamine. It is a liquid, boiling at 277°; specific gravity 1.503 at 12°. Insoluble in water, soluble in acohol and ether.
- (4)  $\beta$ -Naphthyl-chloride,  $C_{10}H_7$ . $CH_2Cl$ , is formed when chlorine acts upon  $\beta$ -methyl-naphthalene at a temperature of 240° to 250°. Melts at 47°, boils at 168°.
- (5)  $\beta$ -Naphthyl-bromide,  $C_{10}H_7$ .  $CH_2$ Br.—Formed when the vapor of bromine with  $CO_2$  gas is brought in contact with  $\beta$ -methyl-naphthalene, heated to 240°. Crystallizes from alcohol in white plates, which melt at 56°.

Anthracene Derivatives.—(1) Monochlor-anthracene, C<sub>14</sub>H<sub>0</sub>.Cl.—When dichlor-anthracene is heated, hydrochloric acid is evolved, having the monochlor derivative. Soluble in alcohol, ether, carbon disulphide, and benzene. Crystallizes in yellow needles, melting at 103°.

- (2) Dichlor-anthracene, C<sub>14</sub>H<sub>8</sub>.Cl<sub>2</sub>, is produced when anthracene is allowed to remain in contact with chlorine, or when the monochlor derivative is similarly treated, being maintained at a temperature of 100°. Freely soluble in benzene, but not readily in alcohol or ether. Forms beautiful yellow lustrous needles, which melt at 209°. Treated with sulphuric acid at a low temperature, dichlor-anthracene-sulphonic acid occurs in solution; this, when heated, yields sulphurous acid, hydrochloric acid, and the anthraquinone-disulphonic acid, which is the immediate base of the artificial alizarine.
- (3) Dibrom-anthracene, C<sub>14</sub>H<sub>8</sub>Br<sub>2</sub>.—Upon agitating bromine with a solution of anthracene in carbon disulphide, this derivative is formed. Difficultly soluble in alcohol, ether, and benzene; hot toluene or xylene answer best. Crystallizes in gold-yellow needles, melting at 221°, and subliming without decomposition.
- 3. NITRO- DERIVATIVES.—By the action of nitric acid upon the hydrocarbons nitro- derivatives are obtained, and one of the most important of these—nitrobenzene—is manufactured in very large quantities for use in the color industry.

- (1) Nitrobenzene, C<sub>6</sub>H<sub>5</sub>.NO<sub>2</sub>, was discovered by Mitscherlich, who obtained it by heating benzene or benzoic acid with fuming nitric acid. It was first brought into trade, bearing the name "oil of mirbane" (artificial oil of bitter almonds), by Collas, and in 1847 a patent for its manufacture from coal-tar was granted to Mansfield. It is obtained by adding a cooled mixture of concentrated sulphuric acid and nitric acid (150:100) to the hydrocarbon and agitating, taking care that the temperature does not go above 50° C. After the addition of the acid is complete, heat is applied, and it is again agitated. The oily layer is removed, washed with dilute alkali, dried, and distilled. Nitrobenzene, when pure, is a pale-yellow fluid, strongly refractive, having the odor of bitter almonds, and a sweet, though burning, taste. Specific gravity 1.208 at 15°; boils at 206° to 207°, and when the temperature is reduced it crystallizes in large needles, which melt at  $+3^{\circ}$ . Nearly insoluble in water, though with alcohol, ether, and benzene it is readily soluble. It is exceedingly stable, and even at a boiling temperature it is not acted upon by either bromine or chlorine. It is poisonous, and, according to Roscoe and Schorlemmer (vol. iii, pt. iii), "especially when the vapor is inhaled; it produces a burning sensation in the mouth, nausea and giddiness, also cyanosis of the lips and face, and in serious cases, which frequently end fatally, symptoms of a general depression."
- (2) Dinitrobenzene, C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub>.—Three isomers of this derivative exist, being obtained when benzene is nitrated with the concentrated acids, as in the preceding case, but instead of being cooled is boiled for a short time, when the product is washed with water, pressed, dissolved in alcohol, from which the meta-nitro body crystallizes, followed upon standing by the paranitro compound. Upon distilling the alcohol remaining in the mother-liquors from the para- compound, a further yield of the meta- body is obtained, finally the ortho-dinitrobenzene, which occurs in small quantity, crystallizes, and is purified by treatment with acetic acid, from which it is deposited in needles, having a melting point of 117.9°. The para- compound occurs in monoclinic needles, melting at 172°, and subliming. The meta-compound finds technical application in the production of chrysoidine and Bismarck brown, and is manufactured on a large scale by adding a mixture of one hundred kilos. nitric acid (specific gravity 1.38) and one hundred and fifty-six kilos. sulphuric acid (specific gravity 1.84) to one hundred kilos. of benzene. When the reaction is over, a separation of the acids (which can be used again) from the product occurs; commercially, the product is washed with warm and cold water, further purification being unnecessary. It crystallizes in needles or rhombic tables, which melt at 98.8°, boiling at 297°. Difficultly soluble in warm water, easily in ether and alcohol.

Nitrotoluene.—(1) Nitrotoluene,  $C_0H_4(NO_2)CH_3$ , occurs in three isomers. The ortho- derivative is a liquid boiling at 223°, and at 23.5° has a specific gravity of 1.162. Does not become solid at 20°. The meta- derivative melts at 16°, boils at 230° to 231°. Specific gravity at 22° 1.168. Para- nitrotoluene, melting point 54°, distilling unchanged at 236°, occurs in colorless prisms. Nitrotoluene, consisting more or

less of a mixture of the three, is manufactured in large quantities and in the same manner as nitrobenzene. Ten parts of toluene are mixed, and continually agitated with eleven parts of nitric acid (specific gravity 1.22) and one part sulphuric acid (specific gravity 1.33). The product is treated with water, and afterwards with caustic alkali; distilled to remove uncombined toluene, and finally distilled with superheated steam. When fractionated, that part passing over at 230° yields, when purified, para-nitrotoluene, and is employed in the production of toluidine, tolidine, and fuchsine. The fraction between 220° and 223° is nearly all ortho-nitrotoluene.

(2) Dinitrotoluenes,  $C_6H_3(NO_2)_2.CH_3$ —a- or ordinary dinitrotoluene is produced when toluene is added to a mixture of fuming nitric and sulphuric acids and boiled; ortho-nitrotoluene is employed for the manufacture also. Crystallizes in needles, which melt at 70.5°; insoluble in water, little soluble in alcohol, ether, or carbon disulphide.  $\beta$ -dinitrotoluene, isomeric with the above, is produced under similar conditions; or it can be made by replacing the amido group of dinitroparatoluidine with hydrogen. Crystallizes in golden-yellow needles; melting point 61.5°.

Trinitrotoluene,  $C_6H_2$ .  $(NO_2)_3CH_3$ .—Produced by the action of nitric and sulphuric acids upon toluene, or dinotrotoluene, and heating for several days.  $\alpha$ -Trinitrotoluene is soluble in alcohol, crystallizing from it in beautiful needles, which melt at 82°.  $\beta$ -Trinitrotoluene crystallizes from acetone in transparent prisms, which melt at 112°, while from alcohol it forms plates or flat white needles.  $\gamma$ -Trinitrotoluene is deposited from acetone in small hexagonal crystals, melting at 104°.

Mononitronaphthalene,  $C_{10}H_7.NO_2$ .—Two isomers exist; the a-compound is produced when ten parts naphthalene, eight parts nitric acid (specific gravity 1.4), and ten parts sulphuric acid (specific gravity 1.84) are combined in a nitrobenzene apparatus. The naphthalene is added in small portions and continually stirred. The product is washed with water, and freed from acid by treatment with alkali. Insoluble in water, easily in benzene, carbon disulphide, ether, and alcohol. Crystallizing in yellow needles, melting at 61°, boiling at 304°. The  $\beta$ - compound is produced when  $\beta$ -nitronaphthylamine is melted with nitrate of potassa. Soluble in alcohol, ether, or glacial acetic acid. Crystallizes in yellow needles; melts at 79°.

a-Dinitronaphthalene,  $C_{10}H_6(NO_2)_2$ , obtained in a similar manner to the above. Difficultly soluble in cold, easily in warm, benzol. From glacial acetic acid it crystallizes in needles, melting at 217°.  $\beta$ -Dinitronaphthalene, isomeric with the above, crystallizes in rhombic plates, melting at 170°.

4. Amine Derivatives.—The amine derivatives of benzene, toluene, and xylene can be regarded as forming one of the most important groups of raw materials from which are obtained the *basic* coloring matters, all of which contain nitrogen. The structure of the amines can readily be seen if we employ ammonia, NH<sub>3</sub>, as the type; in this case there are three atoms of hydrogen. If one of these be replaced by an organic

radical, a primary amine is produced; if two or all three are replaced, a secondary or tertiary amine respectively is formed.

Aniline, or Amido-benzene,  $C_0H_5.NH_2$ .—This substance was discovered by Unverdorben in 1826, who noticed its property of combining with acids to form salts. Runge, subsequently, experimenting upon coaltar, found a volatile substance which, when treated with a solution of bleaching-powder, produced a blue coloration, giving rise to the name kyanol. It was he who noticed that when a drop of the "nitrate of kyanol" was brought in contact with dried cupric chloride, a black spot was formed. Fritsche, later, examined the distillation products of indigo, and found a body to which he gave the name aniline. Aniline was formerly obtained in large quantities by reducing the nitrobenzene with iron fillings or scrapings and acetic acid, but now it is wholly produced with hydrochloric acid, the following reaction showing the change that occurs:

$$\begin{array}{l} \text{(Nitrobenzene.)} \\ \text{C}_6\text{H}_5.\text{NO}_2 + 3\text{Fe} + 6\text{HCl} = \\ \text{(Aniline.)} \\ \text{C}_6\text{H}_5.\text{NH}_2 + 3\text{FeCl}_2 + 2\text{H}_2\text{O}. \end{array}$$

The quantity of acid represented by the above equation is more than sufficient for the purpose, from the fact that ferrous chloride, (FeCl<sub>2</sub>), a reducing agent itself, will act in the reduction of a further quantity of nitrobenzene:

$$C_6H_5.NO_2 + 6FeCl_2 + 6HCl = C_6H_5.NH_2 + 3Fe_2Cl_6 + 2H_2O.$$

Aniline is a liquid, fluid at ordinary temperatures, but when frozen melts at —8°; boils at 182° when pure; specific gravity 1.036; colorless when freshly distilled, but becomes reddish-brown upon exposure to light and air; impurities hasten discoloration. Soluble in alcohol, ether, and benzene in all proportions; in water it is soluble to a slight extent, one hundred parts of water dissolving three parts aniline, while it, in turn, dissolves water to the extent of five per cent.

Aniline forms a series of well-crystallized salts, among which are the hydrochloride,— $C_6H_7$ .N.ClH,—known as "aniline salt," largely employed in the production of black upon cotton; and the sulphate,— $(C_6H_7N)_2H_2SO_4$ ,—of considerable importance.

Methylaniline,  $C_6H_5$ .NH(CH<sub>3</sub>), is obtained by heating aniline hydrochloride or a mixture of aniline and hydrochloric acid with rather more than a molecule of methyl alcohol at 200° C. The product is then converted into sulphate and the easily soluble sulphate of methylaniline separated from the sparingly soluble aniline sulphate. The sulphate is decomposed by an alkali and the free base obtained by distillation. The commercial product contains from ninety to ninety-five per cent. of pure methylaniline. It is a colorless oil, boiling at 192° C., and has a specific gravity 0.976 at 15° C.

Dimethylaniline, C<sub>6</sub>H<sub>5</sub>.N(CH<sub>3</sub>)<sub>2</sub>, is obtained by heating a mixture of

aniline (seventy-five parts), aniline hydrochloride (twenty-five parts), and methyl alcohol, free from acetone (seventy-five parts), in a cast-iron autoclave at from 230° to 270° C. The product is rectified. The yield is about one hundred and twenty parts from the above proportions. It is a colorless oil, boiling at 192° C., and specific gravity 0.96 at 15° C. Solidifies at +5° C. to a crystalline solid. The commercial product is usually nearly pure.

Nitraviline, C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)NH<sub>2</sub>.—Both the m- and the p- nitraniline are used technically. The former is made by the partial reduction of dinitrobenzene; the latter from acetanilid, which is nitrated and then freed from the acetyl group by treatment with steam.

Toluidine, or Amido-toluene, C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)NH<sub>2</sub>, occurs in three isomers, according to the extent to which the nitration of the toluene was originally carried. Ortho-toluidine is produced by the reduction of ortho-nitro-toluene, by the same means as was applied in the case of aniline. It is a fluid, colorless at first, but becoming brown upon exposure. Specific gravity 1.000 at 16°, boiling point 197°; soluble to a slight extent in water (2:100) and in alcohol.

Meta-toluidine, occurring similarly to the preceding, is a liquid. Specific gravity .998, boiling at 197°, little soluble in water, but freely in alcohol and ether.

Para-toluidine is obtained in the form of large colorless leaflets, crystallizing from alcohol. Specific gravity .973, melting point 45°, and boiling at 198°; slightly soluble in water, readily in alcohol and ether. Commercial toluidine consists chiefly of a mixture of the ortho- and parabodies, and containing very little aniline; it is of considerable importance in the color industry.

Xylidine, or Amido-xylene, C<sub>0</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>.NH<sub>2</sub>, homologous with aniline and toluidine, is produced from xylene, as aniline is from benzene,—nitration followed by reduction. Six isomers are obtainable, but the xylidine industrially employed consists of a mixture of five. At ordinary temperature it is a liquid, specific gravity .9184 at 25°, boiling point 212°. From this derivative the beautiful series of xylidine scarlets are produced.

Naphthylamine,  $C_{10}H_7.NH_2.$ —Two isomers exist. For a-Naphthylamine naphthalene is converted into the nitro- derivative as has been described, and equal parts of this body and water are heated to 80°, incorporated with an equal part of iron filings, and reduced with hydrochloric acid. The product is distilled with lime, and finally rectified by further distillation. Nearly insoluble in water, soluble in alcohol and ether; crystalizes in colorless needles or prisms, which melt at 50°, and boil at 300°. Upon contact with the air it acquires a red color, and oxidizing agents cause a blue precipitate to form in solutions of its salts. It finds extensive application in the preparation of several colors of importance.  $\beta$ -Naphthylamine is produced when gaseous ammonia combines with  $\beta$ -naphthol in the fused state; commercially it is obtained by the action of ammonio-chloride of calcium, or ammonio-chloride of zinc, upon the same body, assisted by heat, and the subsequent separation of by-pro-

ducts. It occurs in white or pearly leaflets, odorless, difficultly solub in cold, freely in hot water, and in alcohol and ether. Melting point 112 boiling at  $294^{\circ}$ . Unlike the  $\alpha$ -naphthylamine, it is not acted upon 1 oxidizing agents.

Phenylendiamine,  $C_0H_4(NH_2)_2$ .—Both the m- and the p- compoundance used in practice. The former is obtained by the reduction of m-director trobenzene with iron and hydrochloric acid; the latter by the reduction of amidoazobenzene with zinc-dust in aqueous solution.

 $C_0H_4.NH_2$ Benzidine (diamido-diphenyl), —This base is manufa  $C_0H_4.NH_2$ 

tured on a large scale as the basis of the substantive cotton dyes (s p. 464). For its preparation nitrobenzene is reduced by zinc-dust ar caustic soda in the presence of alcohol. The hydrazobenzene so obtain is heated in the presence of hydrochloric acid to boiling and the bendine precipitated from the solution by the addition of sulphuric acid. forms a grayish-white crystalline solid, fusing at 122° C., and rath difficultly soluble in water.

Diphenylamine,  $(C_0H_5)_2NH$ , is made on a large scale by heating aniline with aniline chlorhydrate in autoclaves to between 220° and 230 It forms a white or slightly yellowish solid, melting at 54°, and has pleasant odor of flowers.

5. Phenol Derivatives.—Phenol, C<sub>0</sub>H<sub>5</sub>OH.—The occurrence of th body has been mentioned under tar products, page 418. It crystalliz in needles, which have the well-known odor of "carbolic acid." Specif gravity 1.08, and melting at 37.5°, boiling at 132° to 133°; soluble water (1:15) and readily in alkalies, alcohol, and ether. It finds exte sive application in the color and other industries, large quantities being consumed in the manufacture of picric acid.

Resorcin, or m-Dioxybenzene,  $C_0H_4(OII)_2$ , is obtained from benzer by fusing the sodium sulphonate of the latter with caustic soda. (S page 444.) Occurs in sweetish, colorless crystals, which, however, even ually become dark colored, melting at 110°, boiling-point, 271°; readi soluble in water, alcohol, and ether. Specific gravity 1.28.

Pyrogallol, or Trioxy-benzene, C<sub>0</sub>H<sub>3</sub>(OH)<sub>3</sub>, is readily obtained fro gallic or tannic acid when the same are heated to 210° to 220°. It can be obtained from benzene, but the above method is more general adopted. Processes for its manufacture are detailed on page 452. Pyr gallol occurs in white leaflets, which melt at 115° and boil at 210 soluble in water, alcohol, and ether.

Naphthols,  $C_{10}H_7$ .OH.—The two derivatives of naphthalene,  $\alpha$ - at  $\beta$ -naphthol, find extensive application in the manufacture of artifici coloring matters. They are prepared from the two isomeric naphth lene sulphonic acids,  $\alpha$  and  $\beta$ , which are discussed under Processes, pag 452.  $\alpha$ -Naphthol occurs as lustrous needles, which melt at 94°, boil a 278° to 280°; specific gravity 1.224; sparingly soluble in hot, insolub in cold, water; soluble in alcohol, ether, benzene, and in solution  $\alpha$  caustic alkalies.  $\beta$ -Naphthol occurs in leaflets, melting at 122°, boiling

from 285° to 290°; solubilities same as for the preceding. Allen (Commercial Organic Analysis, 2d ed., vol. ii, p. 511) gives the following table of the distinguishing characteristics of the two naphthols:

a-Naphthol.	β-Naphthol.						
Crystallizes in small monoclinic needles. Melting point 94°; boils at 278° to 280°. Faint odor, resembling phenol. Volatilizes readily with vapor of water. Aqueous solution becomes dark violet, changing to reddish-brown on adding solution of bleaching-powder. Aqueous solution becomes red, and then violet, on adding ferric chloride.	Crystallizes in rhombic laminæ.  Melting point 122°; boils at 285° to 290°.  Almost odorless. Scarcely volatile with vapor of water.  Aqueous solution colored pale yellow by solution of bleaching-powder.  Aqueous solution becomes pale green on adding ferric chloride.						

- 6. Sulpho- Acids.—This group constitutes an interesting and technically valuable series of bodies, which are obtained by the action of concentrated sulphuric acid upon the hydrocarbons, or upon coloring matters already formed.
- (1) Benzene-sulphonic Acid,  $C_0H_5$ .SO $_3H$ , is readily obtained by heating two parts benzene with three parts sulphuric acid to 100° C., diluting with water, saturating with earbonate of lead, and decomposing with sulphuric acid to liberate the sulphonic acid. The acid is soluble in water and alcohol, and crystallizes in small plates.
- (2) Benzene-disulphonic Acids,  $C_0H_4(SO_3H)_2$ , are (mainly the meta variety) produced when benzene is heated with fuming sulphuric acid to 275°. Employed in the production of resorcin.
  - (3) Toluene-sulphonic Acid, C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)SO<sub>3</sub>H.—No importance.
- (4) Naphthalene-sulphonic Acids,  $C_{10}H_7.SO_3H.$ —Two isomeric bodies are obtained when naphthalene is submitted to the action of sulphuric acid. At temperatures ranging from 80° to 100° the  $\alpha$ -derivative is largely obtained, and at temperatures from 160° to 170° the  $\beta$ -derivative is produced. Their separation is based upon the different degrees of solubility of the lead salts upon concentrating their aqueous solutions,  $\alpha$ -naphthalene-sulphonic acid being soluble in twenty-seven parts water, while the  $\beta$ -acid requires one hundred and fifteen parts.
- (5) Anthracene-sulphonic Acid, C<sub>14</sub>H<sub>8</sub>.SO<sub>3</sub>H, is produced similarly to the above, or by the reduction of sodium anthraquinone-sulphonate with zinc-dust and ammonia.

Phenol-sulphonic Acid, C<sub>6</sub>H<sub>4</sub>(OH)SO<sub>3</sub>H.—Three isomers are known, two, the ortho- and para-, being produced by the direct action of sulphuric acid upon phenol, while the meta- compound must be produced by other means. The ortho- acid is largely obtained when one part of phenol is slowly mixed with one part of sulphuric acid, care being taken to keep the temperature from rising. The para- acid will be obtained if the mixture be heated to 100°. These bodies are much employed as antiseptics under various names; the para- compound, also, in the production of picric acid.

Naphthol-sulphonic Acids.—The two naphthols are easily converte into mono-sulphonic acids upon being heated to 100° C. with concertrated sulphuric acid; disulphonic acids being produced if the temper ture reaches 110° C. β-naphthol-sulphonic acid, C<sub>10</sub>H<sub>8</sub>.SO<sub>2</sub>H.OH. On hundred parts of β-naphthol are added to two hundred parts of sulphur acid (specific gravity 1.84) and carefully heated to 50° or 60°, when two acids result, ordinary β-naphthol-sulphonic acid (known also a "Schäffer's acid," or "acid S") and β-naphthol-a-sulphonic acid ("Bayer's acid," or "acid B"). When converted into their sodius salts they can be separated by treatment with alcohol, in which mestruum the latter acid is more soluble than the former. They are extesively used for the production of the crocein scarlets; and upon nitraticy yield other colors of importance. If the mixed acid and naphthol heated to about 20° C. Bayer's acid will be formed, while the emploment of a temperature about 90° will cause the formation, as the chiproduct, of Schäffer's acid.

Disulphonic Acids of  $\beta$ -Naphthol,  $C_{10}H_5(SO_3H)_2OH$ , are obtaind when the naphthol is subjected to a temperature of 100° to 110° with three times its weight of sulphuric acid (specific gravity 1.84). Upon dilution milk of lime is added, the precipitated calcium sulphate filters off, carbonate of soda added, and the whole evaporated to dryness, as lixiviated with alcohol, when "salt G" (yellow shade) is dissolved fro "salt R," red shade). Ordinarily, after the addition of the carbonate code, the solution is used without further treatment.

Anthraquinone-sulphonic Acid, C<sub>0</sub>H<sub>4</sub>(CO)<sub>2</sub>C<sub>0</sub>H<sub>3</sub>.SO<sub>3</sub>H, is formed when anthraquinone is treated with fuming sulphuric acid at 160° C. The unaltered anthraquinone is separated, the solution neutralized with sod when the white soda salt settles out. The free acid occurs in yellow plate soluble in water and in alcohol. When fused with either caustic socor potash alizarin is obtained (when anthraquinone-disulphonic acid used, either by itself or in the melt, purpurin is produced along with alizarin); anthraquinone-sulphonic acid being employed directly for the production of this most valuable coloring matter.

Sulphanilic (p-amidobenzene-sulphonic) Acid, C<sub>0</sub>H<sub>4</sub>(HSO<sub>3</sub>)NH<sub>2</sub>, made by the action of sulphuric acid upon aniline at about 190° C. used very largely as basis of the manufacture of dye-colors.

Naphthylamine-sulphonic Acids are prepared from naphthylamine l treatment with sulphuric acid and the application of heat. Sever derivatives are produced, which, however, find limited application, main in some patented specialties.

7. Pyridine and Quinoline Bases.—Pyridine, C<sub>5</sub>H<sub>5</sub>N, is regarded as a benzene nucleus (C<sub>6</sub>H<sub>6</sub>) with one of the CII groups replaced by a atom of nitrogen. It is obtained when bone oil or other nitrogen-containing organic bodies are distilled. It possesses a pungent odor, is liquiboils at 116.7°, and is soluble in water; specific gravity .986. A larg number of the pyridine derivatives bear a relationship to the alkaloic

Quinoline (Chinoline), C<sub>0</sub>H<sub>7</sub>N, differs from pyridine in that naphth lene is the base, C<sub>10</sub>H<sub>8</sub>, one nitrogen atom replacing, as before, one

the CH groups. Quinoline is readily prepared by carefully heating in a flask one hundred and twenty grammes glycerine, thirty-eight grammes aniline, twenty-four grammes nitrobenzene (oxidizing agent), with one hundred grammes concentrated sulphuric acid; when the reaction is over, boil for two or three hours, dilute with water, and remove the unchanged nitrobenzene with steam, saturate with caustic alkali, distil, add sulphuric acid and sodium nitrite (NaNO<sub>2</sub>) to destroy any aniline present, make alkaline, and again distil. Quinoline is a colorless fluid, having a penetrating odor, highly refractive, becoming brown upon exposure to the air; boils at 238°; specific gravity 1.094 at 20°.

Quinaldine (a-Methyl-quinoline), C<sub>0</sub>H<sub>6</sub>(CH<sub>3</sub>)N.—Obtained by the action of hydrochloric acid upon paraldehyde and aniline, for several hours, with the aid of heat. It has a faint odor, is fluid, and boils at 238° to 239°. Technically employed, mainly for the production of "quino-

line yellow," cyanine blue, quinoline red, etc.

Acridine, C<sub>13</sub>H<sub>0</sub>N.—Anthracene is the base from which this derivative is obtained by a substitution of a nitrogen atom for one of the CH groups. As in the previous instances many derivatives of the above bodies exist, which have considerable interest, but no technical importance is attached to them as raw materials.

8. Diazo- Compounds.—These form the most extensive, and probably the most thoroughly investigated of the several groups of coal-tar colors. They are produced when nitrous acid (obtained from starch and nitric acid) is allowed to act upon the primary amines of the aromatic series, in which case the following change is noted, assuming aniline nitrate to be acted upon:

$$C_0H_5NH_2.HNO_8 + HO.NO = C_0H_5N=N.NO_3 + 2H_2O.$$
(Diazo-benzene nitrate.)

Aniline hydrochloride, treated in the same manner, will yield diazo-benzene chloride:

$$C_6H_5.NH_2.HCl + HO.NO = C_6H_5N=N.Cl + 2H_2O.$$

The diazo-compounds differ from those of the azo-group in that one of the bonds of the diatomic nitrogen group —N=N— is satisfied with a hydrocarbon radicle, while in the latter it is saturated with an atom of oxygen, nitrogen, bromine, chlorine, etc., or with an acid or basic group. The annexed list of diazo- bodies illustrates the above:

C <sub>e</sub> H <sub>s</sub> N=NCl	. Diazo	-benzer	ne chloride.
$(C_0H_5.N=N)_2SO_4$	. "	"	sulphate.
C <sub>e</sub> H <sub>z</sub> N=N.Br	. "	"	bromide.
$C_6H_5N=N.NH.C_6H_5$	Diazo	amido-	-benzene.

The azo- compounds have the two nitrogen atoms (-N = N -) united, each to a hydrocarbon group; mixed azo- compounds result if these hydrocarbon groups are not identical.

(1) Diazo-benzene Chloride, CoH5.N2Cl, is formed when nitrite of

soda (NaNO<sub>2</sub>) is added to a solution of aniline chloride in the presence of an excess of hydrochloric acid, the solution being kept cool by means of ice. The product finds application in the manufacture of aniline yellow and other colors.

Diazo-amido Compounds result from the action of salts of the diazo-derivatives upon the primary and secondary amines.

Diazo-amido-benzene,  $C_6H_5$ . $N_2$ .NH. $C_6H_5$ , occurs when nitrous acid is passed through a solution of aniline in alcohol; or by adding a solution of sodium nitrite to a mixture of aniline hydrochloride and aniline. Crystallizes in golden-yellow prisms or scales, insoluble in water, easily in ether, benzene, and alcohol; melting point 91°, exploding at a higher temperature.

- (2) Diazo-benzene-sulphonic Acid, C<sub>6</sub>H<sub>4</sub>.N<sub>2</sub>.SO<sub>3</sub> (the anhydride of the sulphonic acid of diazo-benzene).—Sulphanilic acid, C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>.SO<sub>3</sub>H (see p. 445), is dissolved in water, and sodium nitrite added, when the whole is poured into dilute sulphuric acid, which causes a precipitation of the crystals.
- 9. Aromatic Acids and Aldehydes.—The aromatic acids form a class of bodies of considerable importance, derived from benzenes by substituting the carboxyl group CO.OH for hydrogen. The simplest of the series is Benzoic Acid (Benzene-carboxylic Acid), CoH<sub>5</sub>.CO.OH, which, besides finding extensive application in medicine, is also used in the color manufacture. It can be prepared by a number of methods, chiefly by the sublimation of gum benzoin; by treating the urine of herbivorous animals with hydrochloric acid, which causes the hippuric acid to break up, yielding the acid and glycocoll; and from benzotrichloride with water under pressure. It crystallizes in needles or scales, lustrous, and odorless when pure. Specific gravity 1.291, melting at 121°, and boiling at 249°; soluble in alcohol, ether, benzene, etc., sparingly in water.

Phthalic acid (Benzene-dicarboxylic Acid), C<sub>0</sub>H<sub>4</sub>.(CO.OH)<sub>2</sub>.—Three isomers of the above are known, but only the ortho- acid will be considered. It is obtained from naphthalene tetrachloride by heating with nitric acid or more generally at present by treating naphthalene with strong sulphuric acid in the presence of mercury. It occurs in rhombic crystals, specific gravity 1.585, and melting at 2T3°; upon being heated, it is liable to split up into water and the anhydride; soluble in hot water, alcohol, and ether. When a phenol is heated with the phthalic anhydride phthaleïns result; of these, the resorcin and pyrogallol-phthaleïns are the most important, being the bases of the eosins and galleïns and cœruleïns.

Gallic Acid (Trihydroxybenzoic Acid), C<sub>6</sub>H<sub>2</sub>(OH)<sub>3</sub>.CO.OH.—This acid occurs in several vegetable substances,—chiefly gallnuts, sumach, tea, etc. It is ordinarily prepared by heating gallo-tannic acid with dilute mineral acid, or by allowing crushed galls to remain exposed in a moistened state to the action of the atmosphere for some time, when a fermentation takes place, after which boiling with water removes the gallic acid. It yields needle-shaped crystals, sometimes white, but mostly

light brown in color. Specific gravity 1.70. When heated to 220° decomposes, forming pyrogallol (Trihydroxybenzene, C<sub>0</sub>H<sub>3</sub>(OH)<sub>3</sub>) ar CO<sub>2</sub>. Gallic acid is the chief source of pyrogallol, reference to the app cation of which has been made under phthalic acid.

Benzaldehyde (Benzoic Aldehyde), C<sub>e</sub>H<sub>6</sub>.CO.H.—This body, al known as "Bitter Almond Oil," is a colorless liquid, possessing an agreable odor, and high refracting power. Specific gravity 1.063, boiling 180°, difficultly soluble in water (1:300), easily in alcohol and ethe Several methods are employed for the production of this substance; findustrial purposes, benzyl-chloride is boiled with nitrate of copp and water, half of the contents are distilled, when the oil layer is seprated from the distillate and purified. Mercuric oxide has been use instead of the copper salt. It finds extensive application in the color i dustry, also for the production of cinnamic and benzoic acid, and sever derivatives of value.

10. Ketones and Derivatives, Anthraquinone.—The ketones a closely related to the aldehydes, as will be seen from their structure, - CH<sub>3</sub> — CO — H, *Aldehyde*, CH<sub>3</sub> — CO — CH<sub>3</sub>, *Dimethyl-ketone* (actone).

The CO group—carbonyl—is possessed by both classes, but in the aldehydes is united, on the one hand to an alcohol radical, and on the other to an atom of hydrogen. The ketones, however, are distinguished by having two alcohol radicals (alkyls) linked by the CO group.

Benzophenone,  $C_0H_5$ .CO. $C_0H_5$ , is a ketone of the benzene series, an can be obtained by distilling calcium benzoate, or by heating benzor chloride with aluminum chloride and benzene. It occurs in crystals having an aromatic odor, and which melt at 48° to 49°, subliming at 300 Insoluble in water, soluble in alcohol and ether. It is of some importance, together with the amido- and oxy- derivatives, in the manufactur of certain colors.

Acetophenone (Phenyl-methyl-ketone),  $C_0II_5$ .CO.CH $_3$ .—This is mixed ketone, and contains two residues of different hydrocarbons unite to the carbonyl group. Acetophenone can be obtained by distilling mixture of the benzoate and acetate of calcium. It occurs in crystallin plates, melting at 14° to 15°, and boils at 198°.

Anthraquinone,  $C_0H_4 \subset CO$   $C_0H_4$ .—This substance is of the utmos importance in the manufacture of alizarine. It can be obtained by several processes, the simplest of which is probably the distillation of calcium phthalate, or by oxidizing anthracene ( $C_{10}H_8$ ) with bichromate context and sulphuric acid. Anthraquinone is very stable, oxidizing agents having but little effect upon it. When heated it sublimes, yielding yellowish rhombic crystals. Specific gravity 1.425, melting point 273° insoluble in water, but somewhat in alcohol and ether. Upon fusion with caustic alkalies it yields benzoic acid. For use in the alizarine process it must be converted into the sulphonic acid, and this fused with caustic alkali, dissolved in water, and the coloring matter precipitated by mineral acid, and sublimed. (See Process of Manufacture, p. 453.)

## II. Processes of Manufacture.

1. OF NITROBENZENE AND ANILINE.—The commercial production c nitrobenzene is carried out essentially in the following manner, althoug the details may vary in the different works. Sulphuric acid, 66° Bé and nitric acid, 42° Bé ( = seventy per cent. HNO<sub>3</sub>), are mixed together in the proportion of fifteen parts by weight of the former to ten part of the latter, in a lead-lined wood tank (preferably situated above th nitrating apparatus) and allowed to become cold. Three hundred pound of this "nitrating acid" are run into the nitrating apparatus, either b gravity or by pressure, when the benzene is allowed to flow in in a slow steady stream. During the admission of the benzene the temperature which should be maintained between 80° C. and 90° C., is regulated b means of water kept at about 50° C. circulating around the vessel, o stopping the inflow, should the temperature give indication of rising thereby producing the dinitro- derivative. About one hundred pound of benzene are used, although this quantity is subject to change, accord ing to quality. After the nitration is finished, the contents of the vesse are emptied slowly into large tanks, the acid layer being drawn off first and the nitric acid recovered therefrom, and the nitrobenzene, insolubl in the acid, coming last, is immediately poured into a tank containin water, and washed, followed by a wash with caustic alkali, and finall agitated with water.

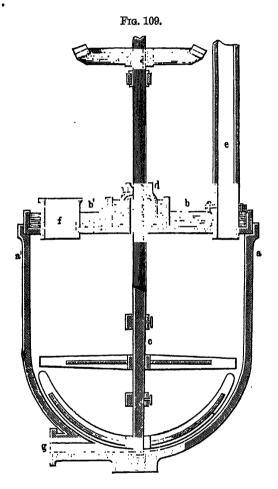
The quantities by weight of the two acids to effectually nitrate eithe benzene, toluene, or xylene, are shown below:

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100 kilos. benzene....120 kilos. nitric acid. 180 kilos. sulphuric acid. 100 " toluene....150 " " " 175 " " " " 100 " xylene..... 90 " " " 150 " " "
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Or, of a standard mixture of one hundred kilos. nitric acid and one hur dred and fifty kilos. sulphuric acid, there will be required for the effecual nitration of one hundred kilos. of the above tabulated hydrocarbor three hundred, two hundred and sixty, and two hundred and twenty-fiv kilos. respectively. The form of nitrating apparatus in use is usuall cylindrical, with a flat or round bottom. Fig. 109 illustrates the latte The cover is provided with several openings: f is for generating charging; e is for the gas exit, while provision is made for the intre duction of the thermometer, and for carrying the agitator shaft. opening for withdrawing the charge is at g. The best plan in arranging the plant is to provide for the acid mixing and nitrating on one floor, c the floor below the washing, and, if desirable, a steam still employed separate the benzene which has not been acted on by the acids, and which is always found dissolved in the nitrobenzene. On the lowest floor, the alkali and final water-wash. If all the operations are performed on or level, a "monte-jus" should be used for the transportation of liquids.

Aniline ("Aniline Oil" of commerce).—Aniline is obtained by the treatment of nitrobenzene with iron filings or scrapings and hydrochler

acid. The apparatus employed are generally of two kinds, vertical and horizontal, the method of working being in each case the same. In the former, the agitator is attached to an upright hollow shaft, so constructed as to provide for the admission of steam to the bottom of the vessel. The cover supports the gearing, and gooseneck for leading the vapors to the condenser, etc. The horizontal form is shown in Fig. 110; the construction provides for agitators attached to a horizontal revolving shaft pass-



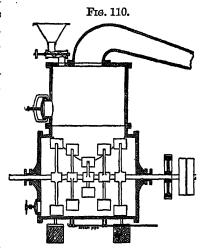
ing through boxes in the heads. Steam enters through the pipes underneath. A steady supply of fine iron is maintained by means of the mechanical feed on the cover. The operation is conducted by adding some of the iron fillings with water, followed by the acid and nitrobenzene; steam is turned on, and, the agitators set in motion, at once the reaction begins, and a mixture of nitrobenzene, aniline, and water appears in the condenser, which is continually returned to the main body in the apparatus; after the reaction has commenced and the dis-

tillate comes over regularly, the iron can be fed steadily, or at unifor intervals. If all the iron is added at once, serious loss is occasioned by reduction of aniline to benzene and ammonia. For a charge of six hu dred kilos, of nitrobenzene, about seven hundred kilos, of iron filing will be required and sixty kilos, of 21° Bé, hydrochloric acid. The solbility of the distillate in hydrochloric acid is noted, until a point reached at which no nitrobenzene separates in an unaltered condition. Formerly it was the general practice to add lime to the tank, and dist off the aniline by means of steam; now the contents are emptied in large tanks containing water and allowed to subside for a day or mor when the lower layer, consisting of aniline, is drawn off and pumpe into a large iron still mounted over an open fire and rectified. Or

hundred parts of nitrobenzene will yield about seventy-five parts of aniline if the process is carefully attended. Ordinarily, the yield will be from seventy-one to seventy-four parts.

2. OF PHENOLS, NAPHTHOLS, ETC.— Phenol.—See Chapter XI., "Coaltar Distillation," p. 418.

Resorcin is manufactured commercially from the soda salt of metabenzene-disulphonic acid, by fusing with caustic soda and subsequent extraction with ether. One hundred kilos, of fuming sulphuric acid are contained in a large cast-iron vessel provided with means for agitating the contents, and into it is gradually allowed to flow twenty-eight kilos, of



benzene; the whole is maintained at a moderate temperature for sev eral hours, and finally raised to about 270° C. to 275° C., after which the contents are transferred to a large volume of water and boiled. Lim is added, the precipitated sulphate removed, and the soluble lime sal decomposed by the addition of the requisite quantity of carbonate o soda; carbonate of lime is precipitated, filtered, and the precipitate free from the excess of solution in the filter-press. This solution is evar orated to dryness in iron pans. For the resorcin melt, sixty kilos, of th above salt and one hundred and fifty kilos, of 76° caustic soda are fuse together for about eight hours at a temperature near 270°; when fusion is finished the melt is cooled, leached out with boiling water, and boile with hydrochloric acid for some time, when the heat is withdrawn, an the solution allowed to become cold, and subjected to the action of ethe or benzene in an extraction apparatus, which removes the resorcin. 'Th benzene is distilled off and recovered, while the crude resorcin remainin is dried at about 210°. Pure resorcin is obtained from the above b distillation.

Pyrogallol.—Several processes are employed for the production o

this substance, all being based upon the use of an aqueous extract of gallnuts or of gallic acid. One process is carried out by heating a glycerine solution of gallic acid to about 200° C., diluting with an equal volume of water, and extracting therefrom the pyrogallol with ether, which is evaporated off and recovered. Another process is to heat one part of gallic acid and two parts water in a closed vessel to 200° to 210° C. for half an hour, when it is cooled, and heated with bone-black, the solution filtered, and evaporated to the crystallizing-point. The crystals are further purified by being distilled in a vacuum.

Alpha- and Beta-Naphthols.—a-Naphthol is manufactured on a large scale in the same general manner as resorcin. a-Naphthalene-sulphonic acid is first prepared by heating naphthalene with fuming sulphuric acid to 90° C., diluting with water, and completely neutralizing with milk of lime, filtering from the magma of sulphate which is passed through a filter-press, the solution of the soluble lime salt decomposed with carbonate of soda, filtered and pressed again and the solutions finally evaporated to crystallization, when, on cooling, the  $\beta$ -naphthalene-sulphonate separates out and is removed. The  $\alpha$ - salt is fused with caustic soda, when the corresponding naphthol is obtained.

 $\beta$ -Naphthol, of much more commercial importance than the preceding, is manufactured similarly. The naphthalene-sulphonic acid is made as above, but at a temperature of 200° C., in order to obtain a large yield of the  $\beta$ -derivative. This is converted into the soda salt, dried, and one part by weight fused with two parts of caustic soda dissolved in the smallest quantity of water, at a temperature of 270° to 300° C.; when the reaction is over, the melt is treated with water, the  $\beta$ -naphthol separated by the addition of hydrochloric acid, filtered, dried, melted, and poured into cylindrical moulds.

3. Of Aromatic Acids and Phthaleins.—Benzoic Acid can be manufactured by several processes and from different sources. For technical purposes the manufacture from benzoin resin and from hippuric acid need not be considered, as it is made almost exclusively on a large scale from the chlorine derivatives of toluene, such as benzal chloride,  $C_0H_5$ .CHCl<sub>2</sub>, and benzo-trichloride,  $C_0H_5$ .CCl<sub>3</sub>. The former, when heated with water or milk of lime under pressure, is changed into benzaldehyde,  $C_0H_5$ CHO, which, however, always has some benzoic acid formed with it as a side-product. The benzo-trichloride, similarly with water or milk of lime, yields benzoic acid according to the reaction  $C_0H_5$ .CCl<sub>3</sub> +  $2H_2O = C_0H_5$ .COOH + 3HCl. The benzoic acid so obtained is almost always contaminated by some chlorbenzoic acid.

Phthalic Acid and Phthalic Anhydride.—The process for their manufacture at present preferred is to heat one hundred parts of naphthalene with fifteen hundred parts of concentrated sulphuric acid and fifty parts of mercuric sulphate. The naphthalene at first goes into solution as a sulpho acid, which, on heating gradually to 300° C., is decomposed with liberation of sulphur dioxide, carbon dioxide, and water, phthalic acid then distilling over. On cooling a mixture of phthalic acid and phthalic anhydride separates out, which is drained and purified. The anhydride

is obtained by acting upon phthalic acid, heated to about 200° C., with carbon dioxide and subliming.

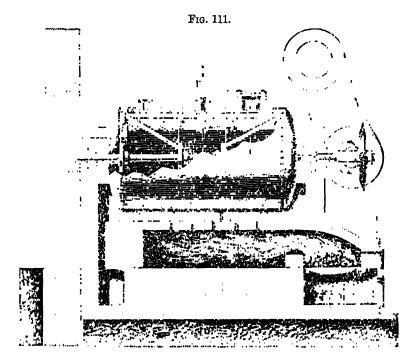
Phthaleins.—When phthalic acid or its anhydride acts upon phenols a class of bodies termed "phthaleins" are formed with elimination of water. Phenolphthalein is manufactured by heating the anhydride, phenol, and sulphuric acid for ten to twelve hours at 120° C.; the sulphuric acid acts only as a dehydrating agent. The melt is boiled with water, the residue dissolved in caustic soda, and the phthalein is precipitated upon the addition of an acid. Resorcin-phthalein, or Fluorescein, is obtained by heating three parts of phthalic anhydride with about four parts of resorcin until the fusion yields no more vapors, and becomes solid at a temperature not exceeding 210° C. The melt is dissolved in dilute caustic soda, with an addition of phosphate of soda and chloride of calcium to remove impurities. The fluorescein is precipitated from the solution by the addition of dilute hydrochloric acid.

4. Of Anthraquinones, etc.—Anthracene in a finely-divided state is suspended in water by agitation, and oxidized by means of potassium bichromate and sulphuric acid at a boiling temperature; allowed to cool, and the anthraquinone is collected on filter-frames, washed with water and dried, and for further purification is treated with concentrated sulphuric acid, and heated to 110° to 120° C., when the dark mass obtained is treated with steam, which causes a dilution, followed by a gradual separation of the anthraquinone in crystals. These are washed with hot water, and afterwards with hot dilute soda to remove organic acids. The yield is about fifty to fifty-five per cent. of the weight of the anthracene used.

Anthraquinone-monosulphonic Acid. (See p. 445.)—This is manufactured by heating one hundred kilos. anthraquinone with one hundred kilos. fuming sulphuric acid (containing forty-five to fifty per cent. anhydride) to 160° C. in an enamelled cast-iron vessel mounted in an oilbath. By varying either the quantity of sulphuric acid or the temperature the alpha- or beta-disulphonic acid will result. The separation of the two latter from the monosulphonic acid is effected by converting the sulphonic acids into lead salts, decomposing these with carbonate of soda, and acting upon the resulting soda salts with dilute sulphuric acid, which has but a slight solvent action upon the monosulphonic acid.

Alizarin.—The alizarin process is carried on in large vessels or autoclaves, mounted as shown in Fig. 111. To the central shaft D agitators are attached, so that the charge may be constantly mixed. F is a thermometer, and the openings in the top to the right are for introducing the charge, and the small one on the left for admitting steam and water. The process is commenced by melting two hundred and fifty to three hundred parts of caustic soda in a small quantity of water, and then adding twelve to fifteen parts of chlorate of potash and one hundred parts of the sodium anthraquinone-sulphonate, when the vessel is closed and the agitator put in motion, the whole being kept at a temperature of 180° C. for two days, when it is allowed to cool, dissolved in a large quantity of water, and the alizarin precipitated by the addition of hydro-

chloric acid. The alizarin is washed to free it from soda salts, passed through filter-presses, and is ready to be either dried and ground, or ground in glycerine to a paste. Neutralizing the soda solution with sulphurous acid instead of with hydrochloric acid enables a recovery of the caustic soda. The yield from one hundred kilos. anthraquinone is one hundred and five to one hundred and ten kilos. alizarine (Schultz). Several processes are employed, varying mainly in the duration of the melt and in the proportion of materials used. Instead of soda, lime is employed, in which case a "lake" is formed.



- 5. Of Quinoline (Chinoline) and Acridine.—Quinoline is produced from nitrobenzene and aniline. Twenty-four grammes of the former and thirty-eight grommes of the latter, with one hundred and twenty grammes of glycerine, are placed in a flask (provided with a return condenser) containing one hundred grammes of concentrated sulphuric acid; when the reaction is over, the contents are boiled for some time, diluted, and the unconsumed nitrobenzene is distilled off; an excess of alkali is added to the solution, and the quinoline distilled off with a current of steam. It can also be obtained from crude quinoline from coal-tar with phthalic anhydride and zinc chloride. Acridine is found along with crude anthracene, from which it is separated by treatment with dilute sulphuric acid, precipitating with chromate of potash, recrystallizing, precipitating by ammonia, dissolving in hot water, from which it separates in crystals on cooling.
  - 6. SULPHONATING.—This general process consists in dissolving the

compound to be changed in fuming sulphuric acid, whereby one or more H atoms are replaced by HSO<sub>3</sub> groups, producing mono-, di-, or trisulphonic acids. Examples of this process are given under Resorcin (see p. 451), the Naphthols (see p. 452), and will frequently be referred to in classifying the artificial dye-colors.

7. DIAZOTIZING.—By the action of nitrous acid upon primary aromatic amines a diazo- compound is formed, as in the following reaction:

$$C_6H_5.N|H_2H|NO_3 = C_6H_5.N=N.NO_3 + 2H_2O. + N|O_2H|NO_3 = C_6H_5.N=N.NO_3 + 2H_2O.$$

These diazo- compounds are susceptible of a great variety of reactions whereby other groups or atoms of elements may be substituted. Thus, by the aid of the diazotizing reaction it is possible to replace a NO<sub>2</sub> or a NH<sub>2</sub> group by OH, H, Cl, Br, I, CN, etc. It is therefore of the greatest importance in synthetic organic chemistry.

The process is carried out in one of two general ways: (a) by con ducting a current of nitrous acid gas through a solution of the substance to be diazotized, the nitrous acid in this case being most conveniently obtained by acting upon starch with concentrated nitric acid in a suitable generator, or (b) by diazotizing in a bath together with the nitrous acid-yielding substance (nitrite of soda generally). In this case the gas is evolved by adding an acid, usually sulphuric, to the solution. Diazotizing is always conducted at a low temperature.

The development of productive values from coal by distillation and working up of the intermediate products to those classed as final products is thus shown by Ost (Lehrbuch der Chem. Technol., 6th ed., p. 555):

1000 kilos, of coal valued at 10 marks yield-

700 kilos. of coke, valued at 10.5 marks; 30 kilos. of coal-tar valued at 0.7 mark; 6 kilos. of impregnating oils valued at 0.25 mark; 15 kilos. of pitch valued at 0.6 mark; 1.1 kilos. of ammonium sulphate valued at 2.75 marks; and 1 kilo. of potassium cyanide valued at 1.3 marks.

30 kilos. of coal-tar valued at 0.7 mark yield-

5 kilos. of benzol valued at 1.1 marks; 2 kilos. of naphthalene valued at 0.16 mark; 0.25 kilo. of anthracene valued at 0.07 mark; and 0.15 kilo. of carbolic acid.

From these intermediate products are obtained:

2.5 kilos. of fuchsine valued at 16 marks; 0.75 kilo. of indigo valued at 6 marks; 0.2 kilo. of alizarine valued at 1.4 marks; and 0.2 kilo. of pieric acid valued at 0.35 mark.

# III. Products.

It would be impossible in the space of this chapter to do more than give a classification of the artificial dye-colors and enumerate a few of the more important under each group. The number of distinct products has already run far into the thousands, and the trade-names by which many

are exclusively known frequently bear so little relation to the chemical names that it would be idle for us to attempt to cover the ground in any other way than by a simple outlining at present. But before taking up this classification it will be well to examine what general principles, if any, underlie the production of a dye-color. O. N. Witt \* has proposed a theory which explains in a very simple way this color formation in the aromatic series. He names a series of radicals or groups which by their entrance alone or with others change a colorless hydrocarbon into a colored compound. These radicals, which he calls "chromophor" groups, are only capable of producing the "chromogens," or parent substances of dye-colors, which chromogens, however, are at once changed into dyecolors of distinct basic or acid character when a salt-forming group Thus, from two molecules of benzene by the entrance of the chromophor group -N=N- is formed azo-benzene, an orange-colored chromogen, but not capable of dyeing silk or wool. When the NH<sub>2</sub> group enters there results, however, amido-azo-benzene, a real dyestuff. from benzene by the entrance of the chromophor group NO<sub>2</sub> is formed the chromogen trinitro-benzene, which by the entrance of the salt-forming group OH becomes trinitro-phenol (or picric acid), a yellow dyecolor.

Witt indicates some eleven of these chromophor groups, to which we shall refer under the appropriate heads in our classification. Of salt-forming groups which change the chromogens to dyestuffs, two are specially to be noted, the amido group NH<sub>2</sub>, which imparts a basic character to the dye-color, and the hydroxyl group OII, which gives the dye-color an acid character. Almost all dye-colors are changed to colorless compounds by the action of reducing agents. The nitro-compounds are changed into the corresponding amido-derivatives, the azo-compounds into hydrazo- or even amido-compounds, while more complex dye-colors are changed by careful reduction into bodies richer in hydrogen, which are known as "leuco" compounds. From these "leuco" compounds the corresponding dye-colors are then formed more or less easily by oxidation. In some cases atmospheric oxidation alone suffices, as with indigo, in others more energetic oxidizing agents, such as lead peroxide, are needed.

Again, the study of dye-colors soon shows that they possess different characters with reference to the ease with which they may be fastened upon the fibre to be dyed or the kind of mordant needed to effect such fastening upon the fibre. We therefore distinguish between basic, acid, and indifferent or neutral dyestuffs. Basic dyes like magneta fasten upon the animal fibre at once, and upon the vegetable fibres after treatment with tannic acid and similar acid mordants. They are used in the form of their salts. The acid dyes are frequently sparingly soluble, and are either brought into soluble condition by forming alkaline salts and sulphonic derivatives, which are then used for dyeing, or they are used with fibres previously mordanted with metallic hydroxides or salts, as in

<sup>\*</sup> Berichte der Chem. Ges., ix, p. 522.

the case of alizarin. In the latter case, however, the color acid forms variety of different colored compounds (lakes) with the different base To the third class (indifferent or neutral bodies) belong indigo-blu and some other substances.

The classification which is now generally accepted is that based in the main upon Witt's chromophor groups, and we will simply note a ferillustrative compounds under each group.

- 1. ANILINE OR AMINE DYE-COLORS.
- (a) TRIPHENYL-METHANE DYES (Chromophor group, —C = ).
  Benzaldehyde Green (or Malachite Green), known also under a variet of other names, is made by the action of benzaldehyde upon dimethy: aniline. The commercial dye is the oxalate or zinc chloride double sal

Brilliant Green (or Solid Green) is the corresponding derivative from diethyl-aniline. The sulphate or zinc chloride salt is used as dye

Magenta (Aniline Red, or Fuchsine) is a mixture of the chlorhydrate of para rosaniline and rosaniline, and is obtained by oxidizing anilin oil with arsenic acid or nitrobenzene. A large number of side-product are obtained in the manufacture of magenta, and have been used unde the names of cerise, cardinal, amaranth, chrysaniline, phosphine, maroor mauvaniline, etc.

Acid Magenta (Fuchsine S) is the sodium or ammonium salt of para rosaniline and rosaniline trisulphonic acids, and is prepared by sulphonating the ordinary magenta.

Aniline Blue (spirit soluble Blue) is a salt of triphenylated para rosaniline, and is made by the action of a large excess of aniline upo rosaniline. If magenta is used instead of rosaniline a reddish-blue is obtained.

Diphenylamine Blue (spirit soluble) is probably the chlorhydrate c triphenylated para-rosaniline, and is made, as the name indicates, from diphenylamine, which is heated with oxalic acid to 120° to 130° C.

Alkali Blue (Nicholson's Blue, Soluble Blue) is the sodium salt of the mono-sulphonic acid of a spirit soluble blue, and is made by sulphonating the latter.

Patent Blue is the disulpho salt of m-oxymalachite green. It color wool a very fast greenish-blue and resists alkalies. Is much used as substitute for indigo carmine.

Hofmann's Violets consist of salts of the ethyl and methyl derivative of rosaniline and pararosaniline, and are made by the action of methyl or ethyl chloride or iodide upon magenta in the presence of caustic sod. It is of historic interest, but has been replaced almost completely k methyl violet.

Methyl Violet is a salt of pentamethyl pararosaniline, and is pr duced by the direct oxidation of the purest dimethylaniline with copp chloride.

Crystal Violet is the chlorhydrate of hexa methyl pararosaniline.

Methyl Green.—This dye is formed by the action of methyl chloriupon methyl violet. The commercial dye is the zinc double chloride. (b) DIPHENYL-METHANE DYES.—Auramine, an important yellow dye, is prepared by heating tetramethyl diamido diphenylmethane with sulphur, ammonium chloride and common salt in a current of ammonia gas.

Pyronine is a red dye obtained by condensing formaldehyde with dimethyl-m-amidophenol and oxidizing the product.

(c) AZINES (EURHODINES AND SAFRANINES).—Chromophor group = N - N =. Neutral Red (Toluylen Red) is a basic dye-color prepared by the action of nitroso-dimethyl-aniline upon m-toluylen-diamine. It is used with cotton after mordanting with tannic acid and tartar emetic.

Safranine (Aniline Rose) is prepared by the oxidation of amidoazotoluene and toluidine, or of p-toluylen-diamine, ortho-toluidine, and aniline. The commercial salt is the chlorhydrate of the safranine base.

Naphthalene Red (Magdala Red) is the compound in the naphthalene series corresponding to the preceding. It is obtained by fusing the chlorhydrate of a-naphthylen-diamine, a-naphthylamine, and amidoazonaphthalene. It forms a dark-brown powder, soluble in alcohol with strong red fluorescence. It is used largely in silk-dyeing and for velvet because of its fine color and fluorescence.

Mauvein (Perkin's Violet) is of historic interest mainly as the first aniline color. It was obtained by W. H. Perkin in 1856 by the oxidation with sulphuric acid and bichromate of potash of a mixture of aniline and toluidine.

Methylene Violet is a reddish-violet dye obtained by the action of hydrochloride of nitroso-dimethyl-aniline upon a mixture of the hydrochlorides of m- and p-xylidine.

Indoines are basic coloring matters dyeing cotton deep shades from dark violet to indigo-blue, fairly fast to light and washing. They are made by combining diazotized safranines with  $\alpha$ - and  $\beta$ -naphthol and conversion into hydrochlorides.

(d) Indulines and Nigrosine.—Induline, spirit soluble (Coupier's Blue, Guernsey Blue, etc.) is prepared by heating amidoazobenzene with aniline to 160° C.

Induline, water soluble (Indigo substitute), is the sodium salt of the disulphonate of the preceding, and is extensively used for silk and wool.

Paraphenylene Blue is a dark blue dye of the induline class obtained by the action of p-phenylene-diamine upon hydrochloride of amidoazobenzene.

Naphthyl Blue is the sodium sulphonate of anilido-phenyl-naphthinduline. Dyes silk blue with a red fluorescence, and is faster to light than the ordinary indulines.

Nigrosine is prepared by heating nitrophenol with aniline and aniline chlorhydrate. The alcohol soluble compound is the simple salt of the base, while the sodium sulphonate forms the water soluble compound.

(e) Aniline Black.—For the preparation of aniline black, aniline chlorhydrate is very carefully oxidized. The dyestuff is not prepared for dyeing or printing, but is fixed on the fibre by an oxidation process

which develops it gradually. It is a very fast black. Quite a varie of oxidizing agents may be used. Potassium chlorate and copper su phate are frequently used in admixture, and vanadate of ammonia is al of special serviceableness in connection with the chlorate. Electrolys of a concentrated solution of an aniline salt will also produce anilin black.

# 2. PHENOL DYE-COLORS.

(a) NITRO-DERIVATIVES.—Picric Acid (Trinitrophenol) is made I nitrating carbolic acid direct with strong nitric acid, or, better, I acting upon phenol-sulphonic acid with strong nitric acid. Forms lightly yellow leaflets or scales, and has been used as a dye for silk and wool.

Naphthol Yellow (Martius Yellow, Manchester Yellow, etc.) is the sodium, potassium, or calcium salt of dinitro-a-naphthol, and is prepare by the nitration of a-naphthol either directly, or after conversion in the mono-sulphonic acid.

Naphthol Yellow S is a sulphonate of the preceding, and is made the nitrating the a-naphthol-trisulphonic acid. The color is faster that pieric acid or the simple naphthol yellow and is more extensively use

Aurantia is the ammonium salt of hexa-nitro-diphenylamine, and made by the nitration of diphenylamine. It was formerly used for wool and silk, but is now used only for leather coloring.

(b) Rosolic Acids.—Rosolic Acid and Aurin (Pararosolic Acid may be prepared from rosaniline and pararosaniline respectively be treatment with sodium nitrite followed by boiling in the presence of suphuric acid. These two coloring matters are no longer of commercial importance.

Yellow Corallin is prepared by heating pure phenol with concertrated sulphuric acid and oxalic acid for some hours until the evolutio of gas nearly ceases. The crude product of the reaction obtained by pouring the melted mass into water is changed into the commercial dy by dissolving it in caustic soda solution and evaporation to dryness.

Red Corallin (Paëonin) is obtained by the action of ammonia under pressure upon the yellow corallin, and represents an intermediate product between aurin and para-rosaniline.

(c) Phthaleins.—Phenol-phthalein is not used as a dyestuff, but an indicator in alkalimetry.

Fluorescëin (Resorcin Phthalëin) is made by heating molecular prportions of resorcin and phthalic anhydride to 195° to 200°. Fluo escëin is not used as such for dyeing, but is converted into the eosin The sodium salt of the fluorescëin comes into commerce under the nan of uranine.

Eosins.—The several halogen substitution derivatives of fluorescëi form the class of dyes known as eosins. Thus, the potassium or sodiu salt of tetrabrom-fluorescëin is the eosin yellow shade, while the co responding salts of tetraiodo-fluorescëin constitute eosin blue shad Methyl and Ethyl Eosin (Primrose) are the methyl and ethyl ethers tetrabrom-fluorescëin. Aureosin is a chlorinated fluorescëin. Saffrosi is the potassium or sodium salt of dibrom-dinitrofluorescëin. Erythros

is the potassium salt of di-iodo-fluorescëin. Rose Bengale is the sodium salt of tetraiododichlor-fluorescëin. Phloxin is the potassium salt of tetrabromdichlor-fluorescëin, and Cyanosine is the potassium salt of the methyl ether of phloxin. Rhodamine is the phthalëin of diethyl-meta-amidophenol. Cyclamine is obtained by the action of iodine upon thionated dichlorfluorescëin. Violamine is obtained by the action of o-toluidine upon fluorescëin chloride and sulphonation of the product. Wool and silk especially are dyed with the eosins, and cotton after mordanting with various metallic salts.

Gallëin is the phthalëin of pyrogallol, and is prepared by an analogous method to that described under fluorescëin. It is very little used in dyeing, but serves for the preparation of

Cærulëin.—This dye is obtained by heating gallëin with twenty times its weight of strong sulphuric acid. Forms a dark amorphous mass, which dissolves in alkalies with a beautiful green color. Cærulëin forms a colorless compound with sodium bisulphite, which is known as Cærulëin S, and is much used in dyeing, as it is easily decomposed by steaming.

- 3. NITROSO AND OXYAZINE COLORS.
- (a) Nitroso Colors (Chromophor group = N-OH).—Gambine is obtained by the action of nitrous acid upon a-naphthol. It dyes iron-mordanted fabrics green.

Dinitrosoresorcin is obtained by the action of nitrous acid upon resorcin. Dyes like the previous color.

Dioxine is obtained by the action of nitrous acid upon dioxynaphthalene. Dyes bright green or brown shades on metallic mordants.

(b) Indophenols and Indamine (Chromophor, N=0).—Indophenol (a-Naphthol Blue) is prepared by oxidizing dimethyl-paraphenylene-diamine and a-naphthol with bichromate of potash and acetic acid Indophenol may be reduced by glucose and caustic soda to a leucocompound known as Indophenol white, which is also sold commercially. When cotton goods are printed with leuco-indophenol, the blue color may be developed in dilute bichromate of potash solution.

Indamines are obtained by heating the indulines with p-phenylene-diamine and p-phenylene-diamine hydrochloride. Dyes deep indigoblue shades on cotton mordanted with tannin and tartar emetic.

(c) Oxyazines (Chromophor 
$$\stackrel{N}{\smile}$$
).—Azurine is obtained by

the action of nitrosodimethyl-aniline hydrochloride upon sym-dioxybenzoic acid. Dyes a violet blue on chrome-mordanted wool or cotton.

Gallocyanine is obtained by the action of nitrosodimethyl-aniline upon gallic acid. It is a gray paste, insoluble in water, but soluble in alcohol with bluish-violet color.

Prune Pure is the methyl-ether of gallocyanine.

Gallanilic Indigo is the sodium bisulphite compound of gallocyanine-anhydride-anilide.

hydrochloride upon  $\beta$ -naphthol. Dyes cotton mordanted with tannin and tartar emetic indigo-blue.

Nile Blue, Capri Blue, and Gallamine Blue are all oxyazine colors obtained by analogous reactions of nitrosodimethyl-aniline or the cor-

responding amidophenol.

Resorcin Blue.—By the action of nitrous acid upon resorcin is produced diazoresorcin, which by the action of concentrated sulphuric acid is changed into diazoresorufin. This yields a hexabrom-derivative, the ammonium salt of which is the commercial dye. It is used for dyeing silk and wool a blue color, which has a red fluorescence, especially by artificial light. By combining with yellow dyes it yields a fluorescent olive color.

- (d) Thiazines (Chromophor S).—Methylene Blue is prepared by oxidizing dimethyl-p-phenylenediamine and dimethyl-aniline in the presence of sodium thiosulphate and zinc chloride. The commercial salt is a zinc double chloride of the sulphur base, called tetra-methyl-thionin.
  - 4. Azo Dye-colors.—Chromophor group, -N = N -.

A. Monoazo Dyes.—(a) Amidoazo Dyes.

Chrysoidine (Diamidoazobenzene Hydrochloride) is obtained by admixing solutions of diazobenzene hydrochloride and m-phenylene-diamine. Forms reddish-brown crystals. Its solution absorbs actinic rays.

Phenylene Brown (Vesuvine) is triamido-azobenzene hydrochloride. Forms a brown powder soluble in water.

Butter Yellow is dimethylamidoazobenzene. This yellow dye is soluble in oils and is much employed for coloring butter, oils, etc.

Acid Yellow (Fast Yellow) is the sodium salt of the disulphonic acid of aniline yellow (amidoazobenzene). It is used largely in dyeing compound shades.

Dimethyl-aniline Orange (Helianthin) is the ammonia salt of dimethyl-aniline-azobenzene-sulphonic acid. Dyes silk and wool a fiery orange. It is also used as an indicator in alkalimetry, as the light yellow color of the solution is immediately turned red by the addition of a drop of hydrochloric acid.

Diphenylamine Orange (Tropwolin OO, Orange IV) is formed by the action of diazobenzene-sulphonic acid upon diphenylamine. Dyes silk or wool a very fine golden yellow.

Metanil Yellow is the sodium salt of phenylamidoazobenzene-m-sul-phonic acid. Forms a yellow soluble powder.

Archil substitute (naphthion red) is made by combining p-nitraniline with naphthionic acid or  $\beta$ -naphthylamine-sulphonic acid.

(b) Oxyazo Dyes.—Sudan G (Aniline-azorescorcin) is a brown powder hardly soluble in water, soluble in alcohol. It is used for coloring spirit varnishes, oils, etc.

Sudan Brown (Pigment Brown) is made by the action of hydrochloride of a-diazonaphthalene upon a-naphthol. It is used for coloring varnishes, soaps.

thalene and  $\beta$ -naphthol. Forms a red-brown powder, soluble in sulphuric acid with fuch sine-red color.

Alizarin Yellow is a yellowish-brown dye made by combining p-nitraniline with salicylic acid.

Fast Brown N (Naphthylamine Brown) is made by combining naphthionic acid with a-naphthol. Dyes wool brown from an acid bath.

Crocein Orange (Ponceau 4GB) is prepared from hydrochloride of diazobenzene and  $\beta$ -naphthol monosulphonic acid. It is a fiery red powder, dyeing a reddish orange on wool.

Orange G is the sodium salt of diazobenzene- $\beta$ -naphthol-disulphonic

acid. It dyes an orange-yellow shade.

Cochineal Scarlet 2R results from the action of diazotoluene upon a-naphthol-monosulphonic acid. It forms a cinnabar-red dye-color.

Azococcin 2R results from the action of hydrochloride of diazoxy-lene upon a-naphthol-sulphonic acid. It forms a red-brown powder, difficultly soluble in water. It is used in silk dyeing.

Wool Scarlet R results from the action of hydrochloride of diazoxylene upon a-naphthol-disulphonic acid. It forms a brown-red powder, soluble in water with yellowish-red color.

Ponceau 2R (Xylidine Red) results from the action of hydrochloride of diazo-m-xylene upon  $\beta$ -naphthol-disulphonic acid. It forms a red powder, easily soluble. It has been used in large quantities as a substitute for cochineal.

Ponceau 3R (Cumidine Red) results from the action of hydrochloride of diazo-m-cumene upon  $\beta$ -naphthol-disulphonic acid. It is used as the preceding, but gives redder shades.

Anisol Red and Phenetol Red are formed by the action of anisidine and amido-phenetol respectively upon  $\beta$ -naphthol-disulphonic acid.

Fast Red B (Bordeaux B) is formed by the action of hydrochloride of diazonaphthalene upon  $\beta$ -naphthol-disulphonic acid.

a-Naphthol Orange (Tropæolin OOO, No. 1) is the sodium salt of p-sulphanilic-acid-azo-a-naphthol. Forms orange-yellow scales, tolerably soluble in water. It dyes silk and wool a reddish orange.

 $\beta$ -Naphthol Orange (Tropæolin OOO, No. 2, Mandarin) results from the action of p-diazobenzene-sulphonic acid upon  $\beta$ -naphthol in alkaline solution. It forms an orange-red soluble powder, and is used largely for wool-dyeing.

Fast Red A (Rocelline, Cerasine, etc.) is prepared by uniting a-diazonaphthalene-sulphonic acid with  $\beta$ -naphthol. It forms a brown-red powder, more soluble in hot than in cold water. It is used largely as a substitute for barwood and orseille.

Azorubin S (Fast Red C, Carmoisin) is the sodium salt of the disulphonic acid of naphthalene-azo- $\alpha$ -naphthol. It forms a reddish-brown soluble powder.

Brilliant Ponceau 4R (Cochineal Red A) and Fast Red D (Amaranth) are both sodium salts of trisulphonic acids of naphthalene-azo- $\beta$ -naphthol, isomeric with each other. The former is a scarlet-red easily soluble powder, the latter a reddish-brown powder.

Roxamine is the sodium salt of dioxyazo-naphthalene-sulphonic aci It dyes wool red from an acid bath and is used as an orchil substitute.

B. DISAZO DYES.—(a) Disazo Dyes from Azo Dyc-colors (Prima: Disazo Dyes).—Resorcin Brown is the sodium salt of a sulphonic ac of resorcin-disazo xylene-benzene. Forms a brown soluble powder.

Fast Brown results from the action of two molecules of α-diaz

naphthalene-sulphonic acid upon one molecule of resorcin.

Acid Brown G is formed by the action of hydrochloride of diaz benzene upon chrysöidin-sulphonic acid. Dyes wool brown in ac solution.

Bismarck Brown is the hydrochloride of benzene-disazo-phenylen diamine. It is much used in coloring leather.

(b) Disazo Dyes from Amido-azo Dyes (Secondary Disazo Dyes).Cloth Red G (Azococcin 7B) results from the action of diazoazo-benzer
upon a-naphthol-sulphonic acid. Forms a brown powder not readii
soluble in water. Used in wool-dyeing, either alone or in connectic
with logwood, fustic, etc.

Brilliant Crocëin (Cotton Scarlet) results from the action of hydrchloride of diazoazo-benzene upon  $\beta$ -naphthol-disulphonic acid. Forn a reddish soluble powder.

Biebrich Scarlet (Ponceau B).—It is the sodium salt of amido-azi benzene-disulphonic-acid-azo- $\beta$ -naphthol. Forms a brown-red fairl soluble powder. Dyes wool and silk in acid bath a red color like coclineal.

Crocein Scarlet 3B (Ponceau 4RB) results from the action of diazazo-benzene-monosulphonic acid upon  $\beta$ -naphthol-monosulphonic acid Forms a red-brown powder dissolving with scarlet-red color. Used i wool- and silk-dyeing.

Bordeaux G is obtained by the action of amido-azo-toluene-monsulphonic acid upon  $\beta$ -naphthol-monosulphonic acid S. Dyeş wool refrom an acid bath.

Naphthol Black is the sodium salt of the tetrasulphonic acid of napl thalene-disazo-naphthalene- $\beta$ -naphthol. Forms a violet-black powde Used exclusively in wool-dyeing.

Wool Black is the sodium salt of the disulphonic acid of a benzen disazo-benzene-p-tolyl- $\beta$ -naphthylamine. It forms a bluish-black solub powder. Dyes a deep blue-black color and is quite stable.

Naphthylamine Black and Anthracite Black are obtained by the ation of disulpho-naphthylene-azo-a-naphthylamine upon a-naphthylemine and diphenyl-m-phenylene-diamine respectively.

Fast Violet is the sodium salt of the disulphonic acid of a naphthelene-disazo-benzene- $\beta$ -naphthol. Forms a dark brown soluble powde Used in wool-dyeing.

Chromatropes 2R, 2B, 6D, etc., are combinations of diazo compound with dioxy-naphthalene-disulphonic acid. They give colors varying fro scarlet to magenta, which on subsequent treatment with a boiling soltion of potassium bichromate change to very fast blacks.

(c) Disazo Dyes from Diamido Compounds (Congo Group, or Be

١,

zidine Dyes).—These dyes are distinguished from all other coal-tar dyes by the readiness with which vegetable fibres may be dyed with them without previous mordanting, so that they are equally applicable to vegetable or animal fibres, and can be used with goods of mixed fibre. They are often called substantive cotton dyes. Their affinity for the fibres indeed goes so far that they can be used like mordants to facilitate the fastening of other coal-tar dyes upon the vegetable fibres.

The commercial products consist generally of the potassium, sodium, or ammonium sulphonates of the dye-color.

Naphthalene Red is the sodium salt of naphthalene-disazo-binaphthionic acid. Dyes unmordanted cotton red from a boiling alkaline bath.

Diamine Gold is the sodium salt of disulpho-naphthalene-disazobiphenetol. It dyes unmordanted cotton yellow.

Chyrsophenine is the sodium salt of disulpho-stilbene-disazo-biphenetol. Dyes like the previous color.

By the diazotizing of this same diamido-stilbene-disulphonic acid are also derived Hessian Yellow, Hessian Purple N and B, and Hessian Violet.

The diazo compound from the molecule of benzidine is similarly combined with a series of compounds to produce the well-known benzidine dyes. Congo G and P, Congo Yellow, Sulphanil Yellow, Brilliant Congo G, Cloth Brown, Diamine Black, Diamine Blue, Diamine Scarlet, Diamine Brown, Diamine Green, and Congo Corinth G.

Congo Red is the sodium salt of diphenyl-p-disazo-naphthionic acid. Forms a reddish-brown powder, soluble in water with fine red color. This solution is so sensitive to acids that a single drop of very dilute sulphuric acid suffices to convert the whole of the liquid to a beautiful blue. It is therefore a valuable indicator in volumetric analysis.

Benzopurpurin is formed by the action of tetrazo-ditolyl chloride upon naphthylamine sulphonate of soda. It is a dark red powder, dissolving easily in water. The scarlet obtained from this dye is not changed by dilute acid as is that from Congo red.

Azo Blue is formed by the action of tetrazo-ditolyl chloride upon  $\beta$ -naphthol-sulphonate of potash. It is a dark blue powder, dissolving easily in water. It is fast to acids but not to light.

Diazotized tolidine yields, besides the two dyes last mentioned, Delta-purpurin 5B, Chrysamine, Azo Blue, and Azo Mauve. Dianisidine and diphenetidine also yield, when diazotized, well-known dyes of this class, such as Benzoaurine, Heliotrope, and Benzo-indigo-blue.

Carbazol Yellow and Naphthol Blue-black are also colors of this class. Supplementary to the Azo Dyes.—Tartrazin is formed by the action of two molecules of phenyl-hydrazin-p-sulphonic acid upon one molecule of dioxytartaric acid. Orange-yellow powder, easily soluble in water. It is a valuable woollen dye, very fast to light and fulling.

Primuline and Ingrain Colors.—Primuline is mentioned here because of its ready convertibility into azo colors (ingrain colors). It is the sodium salt of the sulpho- acid of a sulphated amido- compound, and is formed by the action of sulphur upon p-toluidine. The primuline base

is a yellow powder, very soluble in hot water, and dyes unmordanted cotton direct from a neutral or alkaline bath. Its great importance, however, lies in the fact that as the sulpho-acid of a primary amine it can be diazotized (see p. 446), and then is capable of combining with the whole range of phenols and amines to form azo colors. These operations can readily be carried out upon the fibre, whence the colors so obtained have been called ingrain colors. This diazotizing and developing with the phenol or amine may be effected upon silk, wool, or cotton fibre previously dyed with the primuline base. In this way yellows, oranges, purples, reds, scarlets, maroons, and browns are produced.

When paranitraniline is diazotized we obtain azo-p-nitraniline. If sulphuric acid is added to the compound so formed and the diazo compound admixed with a large excess of salt, the sodium sulphate so produced protects the diazo compound from light, even in the dry state, until ready for use in the dye-bath for dyeing goods padded with

naphthols, naphthylamines, etc.

5. QUINOLINE AND ACRIDIN DYES.—Quinoline Yellow is the sodium salt of quinoline-phthalon-sulphonic acid. It forms a yellow powder, soluble in water or alcohol with yellow color. Used for wool- and silk-dyeing.

Flavaniline is obtained by heating acetanilid with anhydrous zinc chloride for several hours to 250° C. The commercial salt is the hydrochloride of the base so obtained. Was formerly used for wool- and silk-dyeing and for cotton after mordanting with tannin and tartar emetic.

Cyanine (Quinoline Blue) is prepared by treating a mixture of quinoline and lepidine with amyl iodide. It forms a fine blue color, but unstable to light. It is not of importance in textile coloring, but is used in the manufacture of orthochromatic photographic dry plates.

Quinoline Red is obtained by the action of benzo-trichloride upon a mixture of quinaldine and isoquinoline. Is also employed in the manufacture of orthochromatic photographic plates.

Acridine Yellow is the hydrochloride of diamido-dimethyl-acridine. Dyes silk greenish-yellow with green fluorescence, and cotton mordanted with tannin yellow.

Phosphine (Chrysaniline) is, as was before noted (see p. 457), a by-product in the manufacture of magenta, but is probably diamido-phenylacridine. The phosphine of commerce is the nitrate or chlorhydrate of the base chrysaniline. Used at present chiefly in silk-dyeing.

6. ARTIFICIAL INDIGO.—Artificial indigo is now an extensive article of commerce, and in purity and uniformity distinctly excels the natural product. The first important synthesis was that utilizing what is known as "propiolic paste," which is a moist paste containing a definite percentage (usually twenty-five per cent.) of o-nitrophenyl-propiolic acid prepared from synthetic cinnamic acid. Professor Baeyer found that this o-nitrophenyl-propiolic acid when in alkaline solution is readily changed by reducing agents, like grape-sugar, milk-sugar, sulphides, sulphydrates, and especially by xanthogenate, into indigo-blue. The reducing agents act already in the cold in either aqueous or alcoholic solu-

tions. This "propiolic paste" was used for a time in calico-printin being printed on the goods along with the reducing agent, but the decon position of the xanthogenate of soda develops mercaptan, the unpleasa odor of which adheres very persistently to the goods, and the blue col is slightly gray in shade. It has therefore been given up for the preser

Kalle's artificial indigo (due to Baeyer in conjunction with Drewser is prepared by converting o-nitrobenzaldehyde into o-nitrophenyllact ketone by the action of acetone. The product of the reaction is the changed to a soluble compound by treatment with sodium bisulphin and is sold under the name of "indigo salt." This salt, if dissolved water or thickened with any suitable substance and afterwards applicate to woollen fabrics and these passed through a solution of caustic soco of 20° B., causes the full color of indigo to develop.

The o-nitrobenzaldehyde can be made from o-nitrotoluene by dire oxidation with manganese dioxide and sulphuric acid. Considerable i digo is made this way at present, but the amount of toluene available not sufficient to allow of its replacing the whole of the natural indigo.

Following these syntheses comes that of Heumann from phenyl-glyc coll, which, when fused with caustic alkali, yields pseudo-indoxyl, at this is easily changed into indigo by atmospheric oxidation.

Similarly, phenyl-glycocoll-o-carboxylic acid (from chloracetic ar anthranilic acids), heated with caustic alkalies, yields the same result

The method of Heumann was, however, not commercial until a cheap production of phenylglycine-o-carboxylic acid was devised by the Ba ische Aniline and Soda Fabrik. The starting point in this is naphth lene, a cheap and abundant product of coal-tar. Naphthalene on treament with strong sulphuric acid and mercury is converted into phthal anhydride. From phthalic anhydride phthalamide is produced by the action of ammonia and from this anthranilic acid is formed by the action of chlorine and caustic soda. Anthranilic acid and chloracetic acid the react to form phenylglycine-o-carboxylic acid, which by heating wire caustic soda is converted into indigo, or rather into indoxyl-carboxyl acid, the alkaline solution of which is changed by atmospheric oxidatic finally into indigo. This artificial indigo of the Badische Co. is know as indigo pure, and usually occurs as a paste containing twenty per cer of indigo suspended in water.

7. OXYKETONE COLORS (Chromophor 
$$\parallel$$
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(a) Anthraquinone Derivatives.—Alizarin.—This term may I applied commercially to the pure dioxyanthraquinone found in the madder-root and made artificially from anthraquinone-monosulphon acid, or to the two trioxyanthraquinones obtained from anthraquinone disulphonic acid, and known more accurately as anthrapurpurin at flavopurpurin. The first or true alizarin is the blue shade alizarin. This a yellow powder coming into commerce as a ten per cent. or twent per cent. paste. When dried and sublimed it forms splendid orange-recrystals, melting at 280° C. It is insoluble in water and sparingly so

uble only in cold alcohol. Sulphuric acid dissolves it, and on diluting the alizarin is precipitated again unchanged. It acts as a weak acid, and forms alizarates with the alkalies and metallic hydroxides.

Quinizarin, which is made by the condensation of phthalic anhydride with hydroquinone, is an isomer of alizarin and is a dioxyanthraquinone. Both alizarin and quinizarin yield purpurin or trioxyanthraquinone on oxidation. Quinizarin is of no importance as a dyestuff by itself, but is converted into valuable acid dyestuffs on condensation with primary aromatic amines and subsequent sulphonation. Such dyestuffs are alizarin cyanine green and alizarin pure blue.

Anthrarufin is also an isomer of alizarin. It is the parent substance of the important blue acid wool dye alizarin saphirol, which is probably diamidoanthrarufin-disulphonic acid.

Anthrapurpurin (Isopurpurin), as before stated, is a trioxyanthraquinone, but is generally produced along with the preceding compound in the manufacture of commercial alizarin, as both the mono-sulphonic and the disulphonic acids are obtained in sulphonating anthraquinone. Anthrapurpurin is obtained in the purest state by melting pure  $\beta$ -anthraquinone-disulphonic acid with caustic soda and chlorate of potash. It melts at 360° C.

Flavopurpurin is obtained also in the manufacture of commercial alizarin, and can be prepared as sole product by melting a-anthraquinone-disulphonic acid with caustic soda and chlorate of potash. Forms orange-colored needles, melting at over 300° C. A mixture of anthrapurpurin and flavopurpurin with little alizarin constitutes the commercial yellow shade alizarin.

Purpurin is also a trioxyanthraquinone, but differs in its molecular formula from both anthrapurpurin and flavopurpurin, and is therefore one of three isomers. It is not a constituent of commercial artificial alizarin, but is found accompanying true alizarin in the madder-root. It forms red needles, beginning to sublime at 150° C. and melting at 253° C. It is soluble in boiling water with dark-red color.

Alizarin Bordeaux B is a tetraoxyanthraquinone, and is made by oxidizing alizarin with fuming sulphuric acid and saponification of the ether so formed.

Alizarin Cyanine R is penta-oxyanthraquinone obtained by oxidizing the alizarin bordeaux in sulphuric acid with manganese dioxide and heating the intermediate sulphuric ether with dilute acid. Dyes wool mordanted with alumina violet, with chromium blue.

Alizarin Orange (Nitroalizarin) is formed from alizarin by the action of nitrous acid, or by the action of nitric acid of 42° B. upon alizarin suspended in glacial acetic acid. It forms a yellow paste of twenty per cent. dry material. Aluminum salts form an orange color, chromium salts a brown-red shade. Used with silk. wool, and cotton.

Alizarin Red is the sodium salt of alizarin-monosulphonic acid, and Alizarin Maroon is amidoalizarin.

Alizarin Blue is a dioxyanthraquinone-quinoline, and is made by heating  $\beta$ -nitroalizarin with glycerine and sulphuric acid to 90° C.

Dark blue powder, almost insoluble in water. Hence is used either by reduction with zinc-dust, grape-sugar, or similar reducing agent and subsequent atmospheric oxidation, as in indigo-dyeing, or by forming a soluble compound with alkaline bisulphites, designated as Alizarin Blue S. This latter is much faster to light than the original color.

Alizarin Indigo-blue S and Alizarin Green S are similar sodium bisulphite compounds,—the first of penta-oxyanthraquinone-quinoline and the second of tri- and tetra-oxyanthraquinone-quinoline and their sulphonic acids.

Anthracene Brown (Anthragallol) is a trioxyanthraquinone. It is formed by heating benzoic and gallic acids with concentrated sulphuric acid, or by heating pyrogallol with phthalic anhydride and zinc chloride. It comes into commerce as a dark brown paste, and yields very fast shades.

Ruffigallol is a hexaoxyanthraquinone, and is made by the action of sulphuric acid upon gallic acid.

Indanthrene X is obtained by fusing  $\beta$ -amidoanthraquinone with caustic potash. It dyes cotton from a reduced vat (like indigo) bright blue shades which are extremely fast to light.

(b) OXYKETONE COLORS OTHER THAN ANTHRAQUINONE DERIVATIVES.—Alizarin Yellow A is made by the condensation of benzoic acid with pyrogallol, and is a trioxybenzophenone, while Alizarin Yellow C is made by the condensation of acetic acid with pyrogallol in the presence of zinc chloride. It is a gallacetophenone.

Anthracene Yellow is obtained by the treatment of dioxy- $\beta$ -methyl-coumarin with bromine.

Alizarin Black S is the sodium bisulphite compound of naphthazarine (dioxynaphthoquinone).

Galloflavin is formed by the atmospheric oxidation of gallic acid in alkaline solution. Forms a dirty-yellow paste, insoluble in water or hydrochloric acid. Wool mordanted with chromium salts takes a color resembling that obtained from fustic.

8. The Sulphur or Sulphide Colors.

Cachou de Laval was obtained already in 1873 by the fusion of organic substances such as sawdust, bran, etc., with sodium sulphide. It dyes cotton brown.

The fact that diphenylamine and its derivatives fused with sulphur and sodium sulphide yielded a series of colors has been utilized in the preparation of the *Immedial colors*. *Immedial black* produces a fast black upon cotton which can be oxidized on the fibre to *Immedial blue*.

## IV. Analytical Tests and Methods.

In this section it is not the intention to exhaust the subject of the chemical examination of coal-tar colors, but to briefly indicate the more important and characteristic tests. The complete chemical analysis of the artificial organic dyes is very seldom resorted to, the analyst usually determining the *identity* of the coloring matter by means of the tabular

schemes which have been published from time to time as new products have appeared on the market, and estimating the moisture of the sample and such foreign substances as the sulphates of soda, and of magnesia, salt, sugar, starch, and dextrine, sand, etc. Of considerable value in connection with the above is a dyed sample of cloth or yarn, which, although not strictly a chemical test, is one of equal importance, especially for the information of the immediate user of the dye. The recognition of dyes, either by themselves or on the fibre, is often desirable. but this requires considerable care and judgment, from the fact that a very large number are simply mixtures, some with as many as five separate dyes; in such cases the task is almost hopeless. These mixtures are sometimes made at the color manufactory, and again by the local agent; in the latter case, usually to supply some particular shade called for, and generally without any regard to the chemical nature of the constituents; this indiscriminate mixing accounts in a measure for the streakiness and uneven effects noticed in dyeing piece goods and yarn with such colors, which cannot always be detected by dyeing the small test samples in the laboratory.

Fastness to Light is determined by exposing one-half of a dyed skein or piece of dyed cloth to the action of direct sunlight for a definite time, say thirty days or longer.

Fastness to Soap.—A piece of dyed cloth or yarn is worked in a neutral soap lather, washed, dried, and compared with the original.

Comparative Dye-trials.—For this purpose vessels of glass, porcelain, or tinned copper are most convenient,—the latter is the best suited, —and if means can be had to provide heating by steam, it leaves nothing to be desired. When several comparative dyeings are to be made at one time of the same class of samples, one equal temperature is necessary.

For Wool and Silk.—In either case it is best to use a vessel containing about one litre. From twenty to twenty-five grammes of wool (yarn or fabric) and about five to ten grammes of silk answer well for the tests. The quantity of dye used varies, although two standards, representing one per cent. and five per cent. of the weight of the wool or silk, answer, as they give two shades which are convenient for estimating the dyeing value of the sample. To make the test, the color is weighed out carefully, washed into the dye-bath containing water, and brought to the boil, into which the material, previously wetted out, is immersed and kept moving about for a definite time, say twenty to thirty minutes, or until the bath is exhausted of color, when it is withdrawn, washed, dried, and the shade compared with a swatch of the same weight, treated under exactly the same conditions as to temperature, time, etc.

To determine the relative dyeing values of color samples, two solutions of equal value are made of equal (known) weights of the dyes, and two dyeings are made as above, only adding the dye solution to the bath as fast as it is taken up by the fabric; a point will be reached when no more color will be taken up, when the addition must stop, the difference in the volume of the solution remaining, from their original volume, gives the amount used in each test; and as the strength was known,

the relative amounts absorbed by the fabric can be calculated. The above applies equally to silk. No general rule can be given which will embrace the application of the colors to fibres in testing, reference must be had to the various classes of dyes and methods in Chapter XIV.

For Cotton.—Few colors are directly applicable to this fibre without previously mordanting it with suitable substances which will cause the color to remain. In the laboratory, a quantity of cotton is taken (yarn or piece), boiled well in water and immersed in a five per cent. solution of tannin for about twelve hours, when it is removed and boiled in a bath containing two and a half per cent. of tartar emetic for thirty to forty-five minutes, washed, dried, and kept for use. (Other mordants—e.g., tin, iron, alumina, etc.—are used according to the kind of work done in the establishment.) In the matter of printed goods, swatches of cotton cloth, mordanted on one piece with several bases, are made by the printer, and these are then passed through one solution of color, and the effect can be conveniently noticed.

For Woollen Yarn Printing.—Pastes are made up of the color in varying strengths with starch or flour, and with such assistants as may be required, such as oxalic or tartaric acids, stannous chloride, etc., in the following manner: Five grammes of color are taken and mixed with a little water containing dextrine or glycerine, and this is made up to five hundred cubic centimetres with a paste of flour (one pound per Twenty or thirty strands of yarn about a metre long are taken, held at one end, and the color-paste rubbed well in for a space of about six inches with a glass rod or spatula; one-tenth of the colorpaste is emptied out, and the remaining is diluted again to five hundred cubic centimetres, and this is then applied to the yarn, leaving a space of an inch or so from the first. The diluting operation is continued so that the printings on the yarn will represent color in the proportion of 1, .9, .8, .7, etc., giving a range of shades of one color. The yarn so printed is then steamed for about twenty to thirty minutes under pressure, or longer without pressure, washed, and dried. is of much value in matching and valuing shades in tapestry carpets.

By Colorimetry.—This method involves the use of two graduated glass tubes, closed at one end, each of the same diameter, thickness, and length. The standard sample of dye being weighed and dissolved in water, is poured into one tube, while an equal weight of the sample to be tested is poured into the other, and by holding the tubes to the light the depth of color is seen. If one is darker in shade than the other, it is diluted until the shades are equal, when, by knowing the number of cubic centimetres of water added to equalize the tint, the relative strength of the dyes can be ascertained.

Mixtures of Dyes can be detected by sprinkling some of the powder on the surface of distilled water, and noticing the color of the streaks formed as the particles subside, or by dissolving the dye in a little alcohol and water contained in a small exaporating dish or beaker, and immersing therein the end of a strip of white blotting-paper, when, in the case of mixtures, several differently-colored bands are seen on the paper, owing to the fact that the constituents of the mixture do not always possess the same degree of capillarity. These bands can be cut off and separately tested by proper reagents according to the scheme for identification of dyes following. Fractional dyeing has also furnished information of value; usually wool or silk being employed.

Identification of Coal-tar Dyes.—Weingärtner's comprehensive tables, which follow, afford means of determining the group to which a sample of dye under examination belongs. The dyes are divided conveniently into two divisions, basic and acid coloring matters, and the latter into soluble and insoluble in water.

- I. The Dye is Soluble in Water.—Add a few drops of a solution of tannin\* to a solution of the dye, and note the formation of a precipitate, after heating.
- A. Precipitation takes Place.—The color is basic.—A small quantity of the original color is dissolved in water, and reduced with hydrochloric acid and zinc-dust, rapidly filtered, and neutralized with sodium acetate; small strips of filter-paper are immersed in the solution, and exposed to oxidize.

	THE ORIGINAL	Color Reappears	ON THE PAPER	•	The original
Reds.	Oranges and yellows.	Greens.	Blues.	·Violets.	color does not reappear.
FUCHSINE, MAGENTA, ROSENE, With sul- phuric acid, brown. NEUTRAL RED. With sul- phuric acid, green. With caustic sola solution, yel- low-brown precipitate. SAFRANINE. With sul- phuric acid, green. Caus- tic sola, brownish- red precipitate. PYRONINE, ACRIDINE RED. TOLUYLENE RED.	PHOSPHINE, CHRYSANI- LINE. With sulphuric arid, reddish-yel- low precipi- tate. Green fluorescence. Caustic soda, light-yellow precipitate. Soluble in ether with green fluores- cence. FLAVANILINE. With sulphuric acid, dirty yel- low precipi- tate. Soluble in ether with blue fluores- cence. ACRIDINE YEL- LOW. ACRIDINE ORANGE.	MALACHITE GREEN, VICTORIA GREEN, With sulphuric acid, yellow, on diluting with water, green. Ammonia causes gray or red precipitate. BRILLIANT GREEN. With sulphuric acid, same as above, color reap- pears slowly. Ammonia, lit- tle or no pre- cipitate. METHYL GREEN, PARIS GREEN. With sulphuric acid, same as above, color not reappear- ing on dilu- tion. Ammonia, solution de- composed, no precipitate. AZINE GREEN.	METHYLENE BLUE. With sulphuric acid, green. Causic soda causes vio- let-black precipitate. With causic soda, blue- black pre- cipitate. MUSCARINE. Causic soda causes brownish- red precipitate. With tannim, indigo-blue precipitate. CAPRI BLUE. MELDOLA'S BLUE. METAPHENYL- ENE BLUE. INDAMINES.	METHYL VIOLET.  Sulphuric acid causes a yel- lowish-brown coloration; on dilution changes to green and vio- let-blue.  NEUTRAL VIO- LET. Sulphuric acid causes bright violet color; on dilu- tion changes to blue. MAUVEINE. Sulphuric acid causes gray color; on dilu- tion changes to light blue and violet-red. AMETHYST. Sulphuric acid gives green color; blue on dilution. PRINE. PARAPHENYI- ENE VIOLET.	CHRYSÖIDINE. Color, orange. In sulphuric acid, dis- solves to a brownish- yellow solu- tion. VESUVINE. Color, brown, upon silk, orange. In sulphuric acid, soluble to a pale liquid. AURAMINE. Color, yellow. With alkalies, white pre- cipitate. On warming with sul- phuric acid, solution de- colorized VICTORIA BLUE. Color, blue. In sul- phuric acid, brownish- red, changes to bluish- green.

<sup>\*</sup> Twenty-five parts of tannin, twenty-five parts of acetate of soda, and two hundred and fifty parts of water.

# B. No Precipitation takes Place.—The color is acid.

	sh-red. The color of the ammoniacal	paper.	ANTHEACENE DERIVATIVES. ALIZARIN S. Aqueous solu-	lan, brown- lan, brown- lan, brown- lan, brown- lan, delected,  CGERULÉIN S.  Aqueous So- lution, olive mondacal solu- tion, green.  ALIZARIN BLUE S. Aqueous Solution, red- dish-brown, red- dish-brown, green- ish-blue.
	filter-paper.	on platinum foll,	Burns without deflagrating, but with colored vapors. A piece of unmordanted cotton cloth is heated in a solution of the original dye.	The color is removed by the soap solution.  Azo- Derivatives.  The following color reactions are all with sulpharte acid:  Fast Yellow.  Teop zolin OO,—Violet.  Azotal VIII.  Methyl.  BRONZE,—Yellow.  Yellow.
ZINC-DUST.	The color does not reappear on the filter-paper.	The original coloring matter, when heated on platinum foll,	Burns without deflagrating piece of unmordanted co tion of the original dye.	The dyed cloth is treated with a warm solution of sasp. The color remains.  BENZIDINE DERIVATIVES. COROO RED. Aqueous solution. ed. In igdro-cidore acid, blue.  BENZOPURPURIN. Aqueous solution, orange, in concentrated ingroching and sulphuric acid, brown precipitues.  AZOBLUE. Aqueous solution, violet blue.  AZOBLUE. Aqueous solution, yiolet blue.  idon, violet blue. Alkolica change to bloodred.  ERYTHROSIN. Aqueous solution, bloodred.  Golution, bloodred. Ica change solution, bloodred.  ERYTHROSIN. Aqueous solution discussioned.
REDUCE WITH HYDROCHLORIC ACTO AND ZINC-DUST.	The col	The original α	Deflagrates without colored vapors.	NITRO-COLORING MATTERS. PICRIC ACID. AQUEOUS SOlution, greenish-yel- low. No precipitate with hydrochloric acid, Defonates when mixed with carbonate of soda and headen. MARTUS YELLOW. With hydrochloric acid, yel- lowish-white precipi- tate. Soluble in ether. NAPHTHOLY ELLOW. No precipitate with hydro- choric acid. Insoluble in ether. AURANTA. Concentrated squeous solution, red; when diluted, yellow. Alkalies throw down deep-red precipitate.
REDUCE WITH	the filter-paper.	d with hydrochloric acid, h ether.	The ether remains uncolored.	SULPHONATED ROSANI- LINE DERIVATIVES.  ACID FUCESINE, ACID MA- effert., bluish-red. In subplante orad, yellow, changing to red on di- lution.  ACID GREEN Pale green in aqueous solution.  ALIXALI BLUES. Alkelies decolorize; restored by acids.  CHINA BLUE. Aqueous solution, blue. Alkalies have no action.  ACID YOLET. Aqueous solution, violet. Am- monta decolorizes. In sulphuric acid, orange solution. On dilution, gray-violet.  INDULNES, NIGROSINES. Aqueous solution, gray- ish-riolet. Blue precip- itate with hydrochoric cacid. With mamonia, violet-red precipitate.
	The color reappears on the filter-paper.	The squeous solution is acidulated with hydrochloric acid, and ether.	The ether takes up the color.	PHTHALİENS.  BOSIN. With sulpharic acid, solubronnic-acid vapora sare evolved.  Rydrochloric acid, precipitate or ange-colored flakes.  SAFRICENES. Sulpharic acid causes gold-yellow solution. Bytho-bromic acid evolved on heating. With hydrochloric acid, brown flakes precipitated.  PHLOXIN. Same as above. Flesh-colored precipitated with hydrochloric acid, brown flakes precipitate with hydrochloric acid, proposate evolved.  Ross BENGALE. No fluorescence in water. With sulpharic acid, or sange color. On heating, iodine water. With sulpharic acid, or sange color. On heating, iodine decolorized with formation of brown precipitate.  CORALLIN. AURDIN. Brick-red solution. With hydrochloric acid, preliow precipitate. No vapors trum. With hydrochloric acid, yellow precipitate. No vapors on heating.

II. The Dye is Insoluble in Water.—Treat with a five per cent. solution of caustic soda.

Insoluble in seventy per cent. alcohol.	Indigo. Ground fine,	with zinc- dust and a m m o n i a,	vellowish so- lution, pro- ducing blue stains on filter-paper. AMILINE	PRIMULINE BASE.
		s fluorescent.	With thirty-three per cent, soda solution, fluorescence re- mains,	Prinkrose. Alcoholic solution has blue-red color, with yellow fluorescence.  Cyanosin: Alcoholic solution, bluish-red with dark-red fluorescence.
NOT DISSOLVE.	per cent. alcohol.	The solution is fluorescent,	With thirty-three per cent. soda solution, fluorescence disap- pears.	MAGDAIA RED. Alco- hold: solution, blue, with a cinnabar-red fluorescence.
THE DYE DOES NOT DISSOLVE.	Soluble in seventy per cent. alcohol.	The solution is not fluorescent.	With thirty-three per cent, soda solution, no change.	Indopherion. Also- holic solution, blue. On adding hydro- choric acid, becomes brownish-red. Sudan II. And III.
		The solution is	With thirty-three per cent. soda solution, change to reddish- brown.	INDULINES and NI- GROSINES, In alco- lab., subtion green- ish-blue. Agfated with benzel, shows marked brown-red fluorescence. PRENTLAMINE BLIE. Alcohof. Solution deap blue. On add- ing hydrochloric acid, becomes green. No fluorescence. With benzol.
THE DYE DISSOLVES.	solution is filtered, and the zinc-dust, small slips of filter-		The original color does not reappear.	CANARIN. Soda solution, yellow. Insoluble in suphuric acid.  ALIZARIN. Soda solution, blueviolet: charged to red on heating with zinc-dust.  ANTHRAPURPURIN. Fuchsine red in alkalies.  FLAVAPURPURIN. Same.  CHRYSAMIN. In soda solution, orange. In sulphuric acid, fuchsine-red.  NITRALIZARIN. Soda solution, red. Reduced with zinc dim, red. Reduced with zinc dim, red. Reduced with zinc dim. Stains paper indigoblue.  ALIZARIN BLUE. Difficulty soluble in soda to green solution; stains fluer-paper violet.  ALIZARIN BROWN. Soda solution, sirains fluer-paper violet.
THE D.	If necessary, the soda	paper are immersed in the air.	The original color of the solution reap- pears.	GALLOCYANN, Soda solution, violet; sulphuric acid, blue. GALLËIN. In sulphuric acid, blue. CGRULËIN. Soda solution, green: sulphuric acid, green. GALLOFLAVIN. Soda solution, vellow; ALIZARIN BLUE. ALIZARIN BLAGK. RUFFIGALLOL.

Destrine.—This substance is estimated by weighing one or two grammes of the dye in a small tared beaker, provided with a glass rod. The dye is dissolved in a little water, and absolute alcohol added, when the destrine will be thrown down, and adheres closely to the glass. The contents are emptied, and the glass rinsed two or three times with alcohol, dried, and weighed.

Starch.—The presence of this substance must not be taken as an adulterant in every case it is found; owing to its peculiar properties it acts as a drier or absorber of moistness, and hence prevents the caking of the dye. By dissolving a quantity of the dye in water, and allowing the solution to stand in a conical glass for a while, any starch present will subside, the clear liquid is poured off, and the residue repeatedly washed with distilled water and alcohol until no color remains, it can then be examined with the microscope; a drop is placed on a slide with a drop of water, the cover-glass put on, and a drop or two of iodine solution placed on the edge, and allowed to displace the water by the aid of a piece of filter-paper opposite the iodine, will, if starch is present, develop the characteristic reaction,—blue.

Sugar.—Estimated as for dextrine; the alcohol used should be saturated with sugar. Sugar can be estimated in dyes by precipitating the coloring matter with basic acetate of lead, and proceeding as for raw sugar with the polariscope (see page 173), or by inverting and estimating with Fehling's solution (page 175).

Sand and Iron Filings are gross adulterations occasionally met with in dyes from unprincipled dealers. Their presence would have been noticed under the *insoluble matter* determination. Iron filings can be easily determined with a magnet.

A careful microscopic examination of ground and crystallized dyes will throw much light on their preparation; bronze-powder and sugar crystals have been thus found.

Paste-dyes, etc., are best estimated by evaporating a weighed quantity to absolute dryness in a small glass mortar, grind thoroughly, add water, and filter through a tared filter, wash with water, dry, and weigh. If this is not done, trouble will be met; paste-dyes not filtering well if simply diluted with water.

The Examination of Dyed Fibres can well be accomplished by the aid of the following table, which is adapted from those of Hummell,\* of R. Lepetit,† and of Lehne and Rusterholz,‡ and embraces a majority of the more important coloring matters which have found application. The reagents employed are hydrochloric acid (HCl), concentrated, 21° Beaumé, and dilute, one part of acid 21° B. and three parts water; sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), concentrated, 66° B., and dilute, one part of acid 66° B. and five parts of water; nitric acid (HNO<sub>3</sub>), concentrated, specific gravity 1.40, dilute one part of the strong acid and two parts of water; caustic soda solution (NaOH), concentrated, 38° B., and dilute, one

<sup>\*</sup> Hummell, The Dyeing of Textile Fabrics, London, 1885.

part of the strong solution and ten parts of water; ammonia, specific gravity .960; alcohol, ninety-six per cent.; stannous chloride, tin salt (SnCl<sub>2</sub> + 2H<sub>2</sub>O), and concentrated hydrochloric acid equal parts; acetate of ammonia solution, by neutralizing ammonia with pure acetic acid and bringing exactly to 5° B.

The initials or names in parentheses following the names of the dyecolors are those of the manufacturers who furnish the particular dyestuff, and will be readily understood by those accustomed to handle these wares.

A separate column has not been made for nitric acid, but where its action is distinctive it is noted under the head of remarks.

Method of Procedure.—For the testing with concentrated acids and caustic alkalies small watch-crystals are most advantageously used. These are then placed upon white paper in order to be able to observe carefully the changes of color. The concentrated acids are most conveniently dropped from small dropping tubes or pipettes, so that they can be added drop by drop until the fibre is completely covered. After addition of the acids four to five minutes are allowed, and the action is then noted. The watch-crystals are then heated carefully by using a very small flame or placing them upon a steam-coil, but the liquids upon the watch-crystals should not be allowed to boil. After waiting a few minutes and allowing them to cool, water is added to the contents of the watch-crystals.

All the other reactions of the tables are carried out in test-tubes. The fibre is placed in the test-tube, covered with the reagent, and allowed to stand for several minutes, then heated without quite bringing the liquids to the boiling-point, when the action is carefully noted. Finally the liquids are boiled for a short time. The solution is then poured off and caustic alkali or acid, as the case may be, is added, and any change carefully noted. After the tests with concentrated hydrochloric or sulphuric acids the fibres are well washed with water in order to observe whether the original color is thereby restored.

DIFFERMENT OF COLORING MATTERS ON THE FIBRES.  Ons of the dyed fabric, or fibres, are placed in the several reagents, contained in porcelain evaporating dishes, and the reaction noted.
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	1						O161	LLIN	ע ד	A.	LT.	$\mathbb{C}\mathbf{R}$	s.			
	Remarks.			Gives no fluorescent solution on boiling with Al <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> . (Distinction from madder and purpurin.)	Bleaching-powder and chromic acid bleach it. Boiled with Pa/OTT School	becomes violet. HNOs gives yel-	An alkaline solution of KereCye	HNO2 vapor converts it into yel- low nitro-alizarin.	On heating, alizarin-red loses brilliancy and becomes brown-	ish, but regains most of the bril- liancy on exposure to air.	holic solutions give characteristic	"The specific	Nitrous acid, fibre brownish-black. Picric acid, fibre reddish-brown. All these days which	are attached by a hot soap solu- tion.	Nitrous acid, fibre blue-black and violet. Picric acid, fibre dark hrown	
	Alcohol.	But little ex-		No action								Color extracted.	Extracts traces of color.		No reaction.	
	SnCl <sub>2</sub> + HCl.	Color extracted	on boiling.	yellow, liquid bright yellow.								In the cold, so- lution yellow.	Fibre brownish.   1 red, pink, and finally decol.		Fibre blue- black, light gray, finally	- COLOTTOR
and Lyco.	NEOH.	Same as with	restored on exposure.					-							No reaction.	
1	NaOH.	Decolorized in	Fibre and solu-	tion yiolet.							Solution bright c	red. No reaction.			TO TEMENOH.	
	H <sub>5</sub> SO <sub>4</sub> .	Same as with HCl.	Dilute, no action:	concentrated, red color extracted. Concentrated H <sub>2</sub> SO <sub>4</sub> at ordinary	tirely dissolves cotton dyed with	alizarin-red, and the alizarin sepa-	rates out as a floc- culent precipitate,	lected, dried, and			Same as with HCl.		F		solution dark blue; on dilution blue.	-
	HCI.	Bluish-red liquid extracted; color	changed. Dilute, no action;	fibre oright yellow, liquid amber-yellow.							Fibre yellow.	Dilute HCl, fibre	orless.		ń	
	'AME OF COLORING MATTER,	ACID MAGENTA. (B. A. S. F.—R. H. and S.)	ALIZARIN.									BENZOPURPURIN B. (Bayer.)		BENZOPURPURIN		

HNOs gives a dark-blue spot, which changes to brown with a dark-blue border.	Nitrous acid, fibre black; turns black-violet with ammonia. Picric acid, fibre brown.	HNO <sub>8</sub> , brown-violet spot, disap- pearing on washing.	Nitrons acid, fibre dark blue; washed with ammonia turns ma- genta-red.	Nitric acid, blackish-blue spot, original color restored by ammonia.  Nitrous acid, fibre reddish-brown; ammonia does not restore original color, but turns the fibre brownish-purple and the solution blush-purple.	Mirrie and gives at first a dark-blue spot, which changes to bright yellow with a greenish-blue border.		Nitrous acid, fibre violet-black; turns violet-red on the addition of ammonia. Picric acid, fibre brownish-red.	Nitrous acid, fibre reddish-brown; unchanged by ammonia. Picric acid, brown spot.
Little or no action.	Extracts some color.	No action.	Solution scarcely col- ored.	No reaction.	Little or no action.	Extracts some dye.	No reaction.	No reaction.
Fibre decolor- ized.	Fibre brownish- red, becomes decolorized.	Little action in the cold; on heating, fibre is decolorized.	Fibre black, blue, gray, and finally colorless.	Fibre blue- black, blue, gray, and finally color- less.	Fibre decolor- ized.	Fibre first brown, grad- ually color- less.	Fibre dark brown, then lighter, then pink, and finally color-	Decolorized,
No reaction.	No reaction.	Fibre unaltered, solution pink.	Fibre reddish, solution pale pink.	No reaction,		No reaction.	No reaction.	Fibre brilliant red, solution scarcely red- dish.
Fibre dark bluish-red, liquid color-	No action.	Fibre turns slightly brown, solution light pink.	Fibre reddish- blue, solution colorless; color appears on washing.	Little change, solution color- less.	Fibre blue.	No reaction.	No reaction.	Fibre darker, and assumes a blue tint, so- lution pale brown-red.
Fibre and solution green.	Fibre blue-black, solution blue; on dilution purple- violet.	Fibre and solution blackish-violet.	Fibre black, solution dark blue.	Fibre bluish-black, solution dark- blue; turns blue- black on dilution.	Concentrated acid, fibre and solution blue.	Fibre dark brown, solution dirty green; reddishbrown on dilu-	Fibre blue-black, solution dark blue; on dilution at first gray, then brown-red.	Fibre blackish-blue, solution black- violet; on dilu- tion grayish-blue.
Fibre violet, liquid colorless; liquid becomes greenish-hue on standing	Dilute HCI, fibre brown-red, solution colories. Concentrated HCI, fibre black-ish-violet with a reddish titt in	Dilute HCl, no re- action. Concen- trated HCl, fibre dark violet; origi- nal color restored	Dilute and concentrated HCl, fibre black.	Fibre at once biush-black, so- lution colorless.	Fibre at first violet, liquid colorless; on standing, fibre becomes blue, liquid greenish-	Dilute, fibre red- dish-brown; con- centrated, fibre olive-black.	Dilute, fibre brown- red, solution color- less; concentrated, fibre greenish- black.	Dilute, fibre black- violet; concen- trated, fibre blue, solution colorless.
BIEBRICH SCARLET.	Brilliant Congo. (Bryer.)	CARMOISINE. (Bayer.)	CONGO CORINTH. (Bayer.)	Congo Red. (Berlin. Act. Ges.)	Crockin Scarler 7B. (Bayer.)	DELTA-PURPURIN 5B. (Bayer.)	DELTA-PURPURIN G. (Bayer.)	DIRECT RED (Geigy.)

# Red Dyes.—Continued.

Remarks.	Hot water containing a little NH,OH extracts a pink liquid from soluble cesins.	Nitrous acid, fibre violet-black; brown.red with ammonia. Picric acid, fibre brown.	To detect in presence of eosin, extract in boiling alcohol,—this removes eosin, which is then tested; wash the fibre or fabric,	and test for magnula. Fed., Sodium sulphide decolorizes.  To distinguish from orchil and aurin: aurin: aurin: color from material dyed with magnita, but extracts a yellow color from aurin, while from or-color from aurin, while from or-color from aurin, while from or-color from aurin, and from or-color from or-color from aurin, and from or-color f	tained and a decoloring extract of magenta is decolorized with NH <sub>2</sub> OH, while one of aurhi is turned bluish-red. Orchil remains unchanged.  Nitric acid, violet spot; disappears on washing.	Fast to soap, light, and acids of ordinary dyeing strength.	Nitric acid gives a bright yellow spot. Bleaching powder bleaches it. Boiled with a solution of Aly SO <sub>3</sub> and cooling, gives an orange fluorescent solution.
Alcohol.	Soluble eosins In one extracted if well dyed. Spirit eosins tracted by sh.		Little extracted; T solution pink fluorescent.	A bluish-red Si color ex- tracted.	No reaction.	No reaction.	Solution red. N
SnCi <sub>2</sub> + HCi.	Fibre orange- yellow, solu- tion pale yel- low,	Fibre black, then colorless.	Little action; fibre slightly blue.	Almost decolorized; color partly restored on boiling.	Slowly decolor- ized in the cold, rapidly on heating.	boiling. Fibre turns gradually reddish-brown.	Brownish-red, solution smber-yellow.
ин,он.	Fibre yellow, solution yel- low, fluores- cent,	No reaction.	No reaction.	Decolorized.	Same as preceding.	ing. No reaction.	Boiled, solution pale pink, fibre not changed.
NaOH.	Fibre yellow, solution pink, fluorescent.	No reaction.	No reaction.	Fibre paler, afterwards colorless.	Fibre violet, solution red- dish-violet.	tion pink. Fibre dirty dark brownish-red.	Heated, fibre and solution cherry-red.
H <sub>2</sub> SO <sub>4</sub> .	Fibre bright yellow at once.	Fibre black, solu- tion blue; after dilution grayish-	blue. No reaction.	Same as with HCl.	Fibre blackish-blue, solution indigo- blue; reddish-rio- let on dilution.	Fibre black-violet, solution same; becomes red on	dilution. Same as preceding.
HCI.	Fibre pale yellow.	Dilute fibre black, solution colorless.	No reaction.	Fibre and solution yellow: original color restored on washing.	Pibrefirst black -vio- let, finally black, solution pale in- digo-blue.	Fibre and solution red-brown.	Boiled, fibre orange- yellow, solution yellow.
NAME OF COLORING MATTER.	SOSIN A.	TESSIAN PURPLE N. (Bayer.)	"(AGDALA RED.	MAGENTA. (Fuchende.)	Orsellin 2B. (Bayer.)	PRINULINE. (POLYCHROMINE.) (CUPOLA.)	Purpurin.

No action in Extracts some odd: or and action in Extracts some odd: or acid, or ange spot, disappear-odd: or action decomes brown-red: solution		Little or no ac- Nitric acid gives violet spot, which tion.	Fibre decolor- Little or no ac- With nitric acid, same as for Scarized.
Extracts some dye; fluores- cent solution.	Color extracted; red fluores- cence.	Little or no action.	Little or no action.
No action in cold; on heating, solution becomes brown-red; solution solution solution	slightly pink. Decolorized on heating.	Decolorized.	Fibre decolor- ized.
Fibre little   No darker, solution slightly in pink and flub by orescent, solution solution in pink and flub by solution in property in	Solution pink. Same as preced- Decolorized on heating.	Fibre paler.	Little effect.
Fibre little darker, with bluish fint, solution un- colored.	Solution pink.	Nearly decolor- Fibre paler.	Nearly decolor- Little effect.
rick-red, so-   Same as preceding.   Fibre little colorless;   darker, with bluish tink rashing.   solution uncolored.	Concentrated, fibre   Fibre black, changes to green.	tion:	No action.
Fibre brick-red, solution colorless; color restored after washing.	Concentrated, fibre blue.	Nearly decolorized on boiling; much	Fibre not changed No action. on boiling, solution builth-red.
CHODAMIN. (B. A. S. F.)	3afranın.	SCARLET 2R. (M. L. and B.)	SCARLET 3R. (M. L. and B.)

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AURAMIN.	Fibre nearly decolorized, orized, solution colories; on dilution original color restored.		Fibre decolorized, solution colorless; after washing, color parity restored	Fibre pale yel- Gradually de- low, solution colorized in coloriess.		No reaction.	Nitrio acid, white spot; gradually turns orange in the centre.
BRILLIANT YELLOW.	Brilliant Yellow. Concentrated, fibre dark yellow.	Fibre black-violet, solution violet.		Same as preced- Fibre dirty yel- No reaction. ing. nally decolor-	ed- Fibre dirty yel- No reaction. low; grad- inally decolor-	No reaction.	
CHRYSAMIN (Bayer.)	Dilute, fibre pale yellow, concentrated, fibre reddish-brown, solution pink, yellow on dilution.	fibre pale Fibre magenta-red, Fibre dark concen. solution red-vio- orange. own, solu- ndv. solu- ndv. yellow rido.	Fibre dark orange.	Fibre light orange. solu- tion colorless.	Slowly decolor- ized.		Nitrie acid, brown spot; gradually turns reddish.gray.
CHRYSOIDINE.	Fibre red.	Yellow color ex- tracted.	Paler and yellower.	Fibre yellower.	Almost decolor-	Yellow color extracted.	
Chrysophenin. (Bayer.)	Concentrated, fibre blackish-violet, solution scarcely colored.	Fibre brown, then dark red-violet, blue on dilution.	Solution pale yellow; no change to fibre.	No reaction.	Fibre brownish- yellow, then decolorized.	No reaction.	Nitric acid, violet spot.
FAST YELLOW. (B. A. S. F.)	Red.	Fibre brownish-red, solution red.	Solution brown- ish-yellow.	Solution brown- Little or no ac- Fibre bright ish-yellow. tion. decolorized.	Fibre bright red, finally decolorized.	Some color extracted.	Nitric acid, bright red spot.
Hessian Yellow. (Bayer.) (Leonhardt.)	Dilute, fibre lighter, concentrated, fibre blackish-blue, solution violet.	ibre lighter, Fibre dark violet, Fibre dark red, trated, fibre solution red-vio- solution light sh-blue, let, pink.	Fibre dark red, solution light pink.	Fibre dark orange, solu- tion slightly colored.	Pale yellow, gradually de- colorized,	No reaction,	

# Yellow and Orange Dyes.—Continued.

Remarks.	Water extracts the color, BeSO <sub>4</sub> decolorizes the yellow solution. Boiling cyanide of potessium extracts a red color. Loses color when heated on the	fibre.			-	Picrio acid has a bitter taste.  Heated with cyanide of potassium becomes red.  In compound colors, should be extracted with alcohol and tested	with Cyanide as above. Nitric acid, red-brown spot.	Nitrous acid, fibre dark orange, and on addition of ammonia orange- brown.	P-raphidol turns ayea nore rea.	
Alcohol.	Some color extracted.	No reaction.	But little color extracted.	Yellow color ex- tracted.	Little color ex- tracted.	Color extracted.	Some color ex- tracted.	No reaction.	No reaction.	No reaction.
SnCl <sub>2</sub> + HCl.	Fibre and solu- tion decolor- ized.	Decolorized.	Decolorized.	At first fibre becomes deep violet on heating, gradually lighter, and finally decolorized	Nearly decolor- ized,	Decolorized.	Fibre orange- brown, then decolorized.	Little action.	On heating, solution becomes yellow, fibre pale yellow, low.	Decolorized on heating.
NE,OH.	Fibre paler, color ex- tracted on boiling.			Solution slightly yellow, flore unchanged.	Fibre paler and bright yellow.	Fibre paler, color ex- · tracted on bolling.	No reaction.	No reaction.	Little action.	Same as preced- ing. heating.
NaOH.	Fibre orange, solution yel- low.	Fibre deep red.	Fibre dull yel- lowish-red.	No reaction.	Fibre paler and yellower.	Fibre becomes orange, solu- tion yellow.	Fibre dark red- brown, solu- tion scarcely	Fibre orange- yellow, color- less solution.	Fibre at first dark yellow, and gradually decolorized; color restored on	washing. Fibre orange, solution or- ange-yellow.
H <sub>2</sub> SO4-	Same as preceding.	Same as preceding, -bluer.	Bright bluish-red.	Same as preceding.	Solution greenish- yellow.	Decolorized.	Fibre orange- brown, solution dark red.	Fibre dark yellow, then pale yellow.	Same as preceding.	Same as preceding.
HCI,	Decolorized almost completely.	Bluish-red.	Fibre red, solution pink,	Fibre reddish-violet, solution violet.	Fibre nearly decolorized, solution	Color extracted on boiling, solution greenish-yellow.	Fibre reddish- brown, solution same.	No reaction.	Fibre more yellow, solution colorless; on dilution, original color of fibre is restored.	Fibre orange, solu- tion yellow.
NAME OF COLORING MATTER.	<b>Nар</b> нтноі. <u>Yellow.</u>	ORANGE No. 2.	ORANGE NO. 3.	Orange no. 4.	Phosphine,	Picric Acid.	PRIMULINE ORANGE.	PRIMULINE YEL- LOW.	Quinoline Yel- low. (B. A. S. F.)	TARTRAZINE. (B. A. S. F.)

POLUYLENE ORANGE Diluke, fibre pink, R. (K. Ochler & concentrated, fibre of the concentrated, fibre of the concentration of the concent	9.4	Fibre and solution yellow.	Fibre orange, solution color- less,	No reaction.	Fibre at first pink, then de- colorized on heating.	No reaction.	Nitric acid, red-violet spot turns gray. Nitrous acid, fibre grayish, on adding ammonia reddish-gray.
Poluylene Orange G. (K. Oehler & Co.)	Dilute, no reaction; Concentrated, fibre voiet, solution reddish; on dilu- tion fibre and so- lution assume original color.	Fibre magenta-red, solution slightly colored.	Fibre light orange, solution scarcely colored.	No reaction.	Fibre pink, decolorized on heating, solution colorless.	No reaction.	Nitrous acid, fibre turns gray, on adding ammonia becomes dirty yellow.
			Gre	Green Dyes.			
Corruigin. (B. A. S. F.)	Fibre duller, solution claret-red.	Same as preceding, solution dirty yellow.	No reaction.	No reaction.	Fibre brownish- red, solution brown; color gradually re- stored on	No reaction.	Nitric acid, brown spot.
RESORCIN GREEN.	Fibre yellowish- gray, solution	Fibre and solution light brown.	Fibre dark green, solution pale green.	No reaction.	Slight decolor- ization, solu- tion brown.	No reaction.	Nitric acid, yellow-brown spots.
VICTORIA GREEN. (MALACHITE GREEN.)	Fibre and solution bright orange; color restored on washing with	Fibre nearly decolorized, solution bright orange.	Decolorized.	Decolorized.	Fibre almost de- colorized, liquid yellow.	Color extracted.	
			Blı	Blue Dyes.			
ALIZARIN BLUE.	Fibre violet, solution yellowish- red.	Dilute, fibre violet, solution slightly red, concentrated, violet solution.	Fibre bluish- green.	No reaction.	Fibre at first violet, brown-ish-red on heating, solu-	No reaction.	Nitric acid, yellow spot, afterwards brown. Somy and bleaching-powder, no action.
Alkalı Blub.	Fibre greenish-blue, solution almost colorless.	Fibre and solution reddish-brown on standing.	Fibre reddish- brown, after- wards decol-	Decolorized.	Fibre not changed, col- orless solu-	Color extracted by absolute al- cohol.	Nitric acid gives a light-green spot with black border.
AZO BLUE. (Bayer.)	Concentrated fibre, blackish blue,	Fibre bluish-black, blue solution.	Fibre cherry- red, solution	Fibre violet-red, pink solution.	Fibre, blue- black, slowly decolorized	No reaction.	Picric acid, fibre blackish-brown.
Basle Blue.	Fibre dark-gray, so- lution yellow, blue on dilution	Fibre blue black, green, finally yel- low, solution yel- low, blue on dilu- tion.	Fibre darker.	No reaction.	No reaction.	Solution pale blue.	Nitric acid, black spot,

Blue Dyes.—Continued.

JAME OF COLORING MATTER.	HOI.	H <sub>2</sub> SO <sub>4</sub> .	NaOH.	NH4OH.	SnCl <sub>2</sub> + HCl.	Alcohol.	Кетагка.
SENZOAZOMINE G. (Bayer.)	Fibre blue-black, colorless solution.	Fibre black-blue, solution greenish- blue, reddish-blue	Fibre dark red, solution pink.	Fibre dark- violet, solu- tion cherry-	Decolorized.	No reaction.	Boiled with soap, solution turns blue.
INDOPHENOL BLUE.	Fibre grayish-	on ditunon. Same as preceding.	No reaction.	No reaction.	Decolorized.	Blue color ex-	Heated with olive oil, purple color extracted.
INDULINE.	brown. Fibre violet, solution deep blue.	Solution dark blue.	Red-violet color extracted, zink-dust added decol- orizes solu- tion; violet color restored by exposing the filtered so- lution to the	Same as preceding.	Extracts a violet or green color.	Bluish-violet color ex- tracted.	Induline NN is not changed by bleaching-powder. Nitric acid gives a dark bluishgreen spot.
Methylene Blue.	Fibre nearly decolorized, solution bluish-green.	Fibre and solution green.	sir. Fibre bluish- violet.	No action.	Decolorized.	Greenish-blue color ex- tracted.	Nitric acid, green spot. Bleaching-powder changes it to green, and finally decolorizes it. On cotton it is faster than most ani- lines, resisting action of soaps. light, and weak bleaching-pow- light, and weak bleaching-pow-
Naphthylene Blue G. (Bayer.)	Fibre brownish-vio- let, solution brown-orange.	Fibre brown-black, solution dark brown, blue on dilution.	Fibre brown, so- lution brown- orange.	Fibre brownish- violet, solu- tion pink	Fibre decolor- ized.	Solution pale violet.	der. HCl vapors change color of fibre to a chocolate-brown.
			vio	Violet Dyes.			
ALIZARIN.	Fibre and solution dull yellow.	Same as preceding.	Fibre bluer,	No reaction.	Same as with HCl.	No reaction.	Destroy color by boiling with HCJ, wash, and add NaOH; the aliza- rin on the fibre is dissolved with
Azo-Violer.	Dilute, fibre bluer, concentrated, fibre blackish-blue, solution color- less.	Fibre black-blue, solution blue- green.	Fibre red, solution colorless.	Fibre dark vio- let, solution pale magenta- red.	Fibre slowly de- colorized.	No reaction.	purple conc. Purple cond, fibre black. Dilute acetic acid, fibre blue,

FAST VIOLET.	Fibre blue-black.	Fibre black, solution gray-blue, greenish-blue, finally red on di-	Fibre black- blue, solution pale violet.	Fibre un- changed, solu- tion pale violet.	Fibre decolor- ized.	Little action.	Nitric acid, blue-black spot.
GALLOCYANINE.	Unchanged.	Fibre dark blue, solution intensely blue, magenta-red	Fibre black- violet, solu- tion dirty	Same as preceding.	Fibre gray, solution colorless.	No reaction.	Nitrous acid, fibre dirty gray-violet, solution blue-green, green, finally yellow.
HELIOTROPE.	Dilute, fibre dark violet, concen- trated, fibre black- blue, solution light, blue, violet	on dilution. Fibre black-blue, solution blue.	Fibre dark red, solution color-less.	No reaction.	Fibre dark gray, slowly decol- orized.	No reaction.	Nitrous acid, fibre greenish-gray, washed and treated with anmonia turns bluish-orange, solution pale brown. Picric acid, fibre dark brown.
METHYL VIOLET.	on dilution. Fibre yellowish- brown, liquid amber-yellow; on diluting with water yiolet color	Same as preceding.	Fibre at first pale reddish- violet, after- wards decol- orized.	Fibre pale lilac, nearly decol- orized.	Fibre green, nearly decolorized on standing, solution yellow-	Color extracted.	
Muscarine.	restored. Fibre blue-black, solution dirty- blue.	Fibre greenish- black, solution greenish, dirty violet on dilution.	Fibre brownish- black.	Fibre violet- blue, solution pale violet.	Fibre blackish; on heafing, blue, green, finally yel- lowish-gray.	No reaction.	Nitric acid, black spot.
			Bro	Brown Dyes.			
ALIZARIN.	Fibre brownish- orange; color re- stored by ammo-	Same as preceding.	Action slight, fibre bluer, solution tinted	Unchanged.	Same as with HCl.	No action.	
Benzo-Brown. (Bayer.)	nia. Dilute, fibre reddish- brown, concen- trated, fibre darker, solution	Fibre brown-black, solution dark brown.	oner. No reaction.	No reaction.	Fibre lighter and yellowish, solution brownish-	Little color ex- tracted.	
BISMARCK-BROWN.	purple-red. Fibre reddish- brown, solution	Same as preceding, darker.	Fibre brownish- yellow.	Fibre un- changed, solu- tion brown	Almost decolor- ized.	Red or pink color ex-	Boiling water extracts color, glacial acetic acid more so, with yellowish-crean fluorescence
FAST BROWN RG. (Berlin. Act. Ges.)	Fed. Fibre dark redviolet, solution violet; on dilution tion fibre becomes	Same as preceding.	Fibre brilliant dark red, solu- tion cherry- red.	Same as preceding.	Fibre darker, and quickly decolorized on boiling.	No reaction.	Nitric soid, black spot, quickly turning to light red-brown.
NAPHTHYLAMINE BROWN.	brown again. Fibre brownish- yellow, solution orange.			Fibre yellow.	Fibre purple, solution pale pink.	Solution bluish- pink.	

Black Dyes.

AME OF COLORING MATTER.	HCI.	*70S*H	NaOH.	NH4OH.	SnCl <sub>2</sub> + HCl.	Alcohol.	Remarks.
LIZARIN BLACK. (B. A. S. F.)	Fibre unchanged, solution pale greenish-blue.	Same as preceding.	Fibre un- changed, solu- tion pale blue.	No reaction.	No reaction in cold; fibre brown on boiling; solu-	No reaction.	Nitric acid, after a while dark olive-green spot.
NILINE BLACK.	No action, or color becomes greenish- black; restored by alkalies; acid	Same as preceding. No action.	No action.	No reaction.	tion yellow. Fibre greenish- gray; color re- stored by am- monia.	Brownish-red color ex- tracted.	Bleaching-powder changes color to brownish-red; weak oxidizing agents have no action.
[APHTHOL BLACK. (M. L. and B.)	solution brownish. Fibre unchanged, solution reddish.	Fibre unchanged, solution olive- green.	Fibre un- changed, solu- tion pale red.	No reaction.	Boiling, fibre No reaction. light green, blue after	No reaction.	Nitric acid, brown spot after a time. This dye is a mixture.
ESORCIN BLACK.	Fibre drab, solution orange-brown.	Fibre and solution brown.	Fibre un- changed, solu-	No reaction.	Fibre and solu- tion light	No reaction.	Nitric acid, brown-yellow spot.
Vool Black. (Berlin, Act. Ges.)	Fibre unchanged, solution light blue, pink on dilution.	Same as preceding	non green. No action in cold; dark violet on boiling; solution violet.	No reaction.	Fibre decolor- ized.	No reaction.	Nitric acid, light red-brown spot.

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### V. Bibliography and Statistics.

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### STATISTICS.

1. CRUDE MATERIALS OF THE COLOR INDUSTRY.—Schultz (Chemie des Steinkohlentheers, 1900, 3d ed., p. 9) states that the present production of coal-tar throughout the world is as follows: England, 660,000 tons; Germany, 160,000 tons; France, 80,000 tons; Belgium, 50,000 tons; Holland, 30,000 tons; America, 120,000 tons; total, 1,100,000 tons.

The yearly production of benzol and toluol from coal-tar and cokeoven gases was estimated by Dr. H. Brunck in 1901 to be from 25,000 to 30,000 tons, of which benzol made up four-fifths. Of this production Germany furnished at that time one-third, but the proportion has probably increased since.

The same authority estimated the yearly production of naphthalene to be from 40,000 to 50,000 tons.

The German production of phenol and cresol in 1902 was estimated by Witt (Die Chem. Industrie des Deutschen Reiches, 1902, p. 199) to be from 4400 to 4800 tons per annum, of naphthalene to be about 17,000 tons, and of anthracene to be from 4400 to 4800 tons.

2. GERMAN COAL-TAR COLOR STATISTICS.—The German trade in aniline oil, aniline salts and other crude coal-tar products was:

	1900.	1902.	1904.	1905.	1907.
Imports in tons	1,241	1,233	2,099	1,624	137
Value in marks	1,120,000	1,130,000	1,890,000	1,460,000	130,000
Exports in tons	12,613	15,969	16,756	19,421	8,704
Value in marks	11,350,000	14,690,000	20,110,000	23,890,000	8,050,000
(Gus	stav Müller. Die	Chemische I	ndustrie. Berli	ı. 1909. p. 3	78.)

The German trade for the same years in aniline and other unspecified coal-tar colors was:

	1900.	1902.	1904.	1905.	1907.
Imports in tons	1,174	1,179	1,461	1,743	2,054
Value in marks	3,820,000	3,650,000	4,240,000	4,790,000	5,240,000
Exports in tons	23,781	28,805	30,831	36,570	43,716
Value in marks		89,300,000	88,590,000	100,650,000	112,500,000
		•	(1	hid n 379 )	

The German trade in alizarin and alizarin colors in recent years has been:

	1900.	1905.	1907.
Imports in tons	39	79	53
Value in marks	40,000	110,000	100,000
Exports in tons	8,591	9,339	10,442
Value in marks1	1,170,000	15,530,000	23,430,000
	•	(Thid.,	n. 377.)

The German trade in indigo was as follows:

	1902.	1903.	1904.	1905.	1907.
Imports in tons	527	291	260	197	127
Value in marks	3,690,000	1,790,000	1,350,000	1,200,000	1,080,000
Exports in tons	5,284	7,233	8,730	11,165	16,350
Value in marks		20,690,000	21,660,000	25,720,000	42,580,000
			· /T	hid. p 375 )	

The value in marks of the coal-tar colors exported by Germany in recent years as summarized is as follows:

1900.	1905.	1907.
Alizarin dye colors.	15,500,000	9,630,000 13,800,000
Indigo 9,360,000	25,700,000	42,580,000
Aniline and unspecified coal- tar colors	100,700,000	112,480,000
97,820,000	141,900,000 (Ibid.,	178,490,000 p. 380.)

To these may be added the totals for the two following years, viz.:

For 1908, 208,654,000 marks, and for 1909, 235,354,000 marks.

(Fischer's Jahresbericht der chem. Tech., 1910, p. 583.)

### 3. United States Importations of Dye-colors.

	1908.	1909.	1910.
Alizarin and alizarin dyes in pounds 3,9	64,126	3,749,869	3,023,348
Value \$7		\$1,215,700	\$647,944
Aniline salts (pounds)	07,790	6,132,517	5,866,982
Value \$4	62,332	\$543,538	\$515,623
Coal-tar colors and dyes valued at\$4,8		\$5,901,842	\$6,011,054
Indigo (pounds) 6,0		8,249,972	7,538,689
Value\$1,0	58,354	\$1,400,286	\$1,195,942
		ation U. S	1910.)

### CHAPTER XIII.

### NATURAL DYE-COLORS.

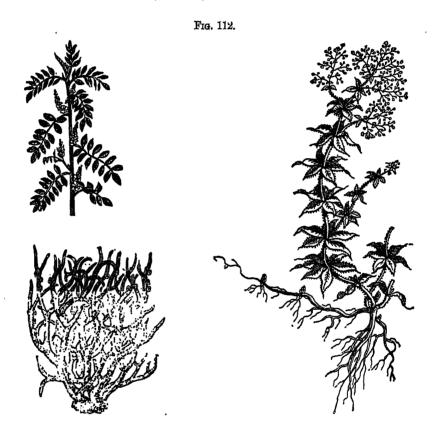
### I. Raw Materials.

THE raw materials to be described here are a series of vegetable dyes coming into commerce partly as compact heart woods and roots and partly as masses of separated coloring matters, together with a few dried animal remains yielding coloring matters. We shall take them up most conventiently in groups according to the colors yielded.

### A. RED DYES.

- 1. Brazil-wood and Allied Woods (syn. Rothholz, Bois de Brésil).— The various species of Casalpinia yield woods which appear to contain a common chromogen, brasilin, C<sub>16</sub>H<sub>14</sub>O<sub>5</sub>. This seems already in the wood to be changed in part into the corresponding coloring matter. brasilëin, C<sub>16</sub>H<sub>12</sub>O<sub>5</sub>. And the change may be made complete by oxidizing the alkaline brasilin solution in the air by acting upon a hot solution of brasilin with an alcoholic iodine solution. Liebermann and Burg ascribe to the crystals of brasilin the formula  $C_{16}II_{14}O_5 + H_2O$ , and call attention to the fact that it bears the same relation to hæmatoxylin,  $C_{16}H_{14}O_6$  (see p. 496), that alizarin bears to purpurin. known varieties of the wood are known by the following special names: Pernambuco-wood, from Casalpinia crista, grown in Brazil and Jamaica. yellowish-red in the interior, becoming red and reddish-brown on the surface. Brazil-wood, from Casalpinia Brasiliensis, grown in Brazil, as well as the Antilles and Bahamas, is brick-red in the interior, becoming brown-red on the surface. It is inferior in coloring power to Pernambuco-wood. Sapan-wood, from Casalpinia sappan, grown in Siam, China, Japan, Ceylon, and the Indian Archipelago, is somewhat lighter in color than the other varieties. It is yellowish-red in the interior and bright red on the surface. Lima-wood, or Nicaragua-wood, from Cæsalpinia bijuga, is grown in Central America and the north coast of South America. The Santa-Martha-wood of Mexico and Peach-wood are by some writers considered as of the same species as Nicaraguawood, and by others are derived from Casalpinia echinata. They have a dirty-red color in the interior, becoming paler on the surface. Bahiawood, California-wood, and Terra-Firma-wood are other less known varieties of the same class.
- 2. Sandal-wood, Caliatur-wood, Bar-wood, and Cam-wood (syn. Santelholz, Bois de Santal rouge) form another group of woods which are alike in many particulars and contain probably the same coloring matter, santalin, C<sub>15</sub>H<sub>14</sub>O<sub>5</sub>. They differ as a class from the Brazil-woods in their more resinous characters, and are often known as "close woods"

in contrast to the others as "open woods." The Sandal-wood (Red Sanders), from *Pterocarpus santalinus*, is grown in the East Indies, Ceylon, and Madagascar, and is a very hard and heavy wood, dark brown on the surface and blood-red in the interior. Caliatur-wood comes also from the East Indies, and though used as a substitute for the sandal-wood is considered as a distinct variety. Sandal-wood is said to contain some sixteen per cent. of santalin. Bar-wood, from *Baphia nitida*, comes from Sierra Leone, Africa, and is a dark-red wood, containing



twenty-three per cent. of santalin. Cam-wood (or Gaban-wood) is supposed by many to be the same as bar-wood, but by others is ascribed to species of *Peterocarpus*. It comes, like bar-wood, from the west coast of Africa. Madagasear-wood is a minor variety resembling Caliaturwood.

3. Madder (syn. Krapp, Racine de Garance) is the dried and broken root of the Rubia tinctorium and allied species. It grows wild in Asia Minor, Greece, and the Caucasus, and has been cultivated in France, Alsace, Silesia, Hungary, Holland, etc. The appearance of the plant may be seen from Fig. 112, in which it forms the right-hand illustration.

In the Levant, the five- to six-year-old plants are plucked, in Europe, those two to three years old. While the Turkish madder (known as Lizari or Alizari) was the earliest in use, the French variety grown in the neighborhood of Avignon, in part upon marshy soil (palus) and in part upon soil containing lime (roseé), has long been considered the best. Other varieties are the Dutch or Zealand madder, the Alsatian, the Silesian, and the Russian madder. That which has not been freed from the brown outer crust before grinding is inferior to that which has been so freed, and which is known as "crop-madder," while the impurest variety, obtained by grinding the rootlets, crusts, and woody parts of the roots, is called "mull-madder."

From the madder-roots are also prepared by fermentation and filtration of the separated dye-colors the commercial extracts known as "madder flowers" and "guarancine." One hundred kilos. of madder will yield fifty-five to sixty kilos. of madder flowers.

The tinctorial value of the madder depends upon the existence of the two coloring matters, alizarin,  $C_{14}H_8O_4$ , and purpurin,  $C_{14}H_8O_5$ , both of which have been mentioned under the artificial dye-colors derived from anthracene. (See p. 466.) These are not found free in the growing plant, but combined as glucosides and other compounds easily decomposable by fermentation. As a nitrogenous and soluble ferment crythrozym is present; so soon as the solutions of madder extract are exposed to the air the ruberythric acid (or alizarin glucoside) is decomposed into alizarin and dextrose and the pseudo-purpurin (or naturally occurring purpurin-carboxylic acid) is decomposed into purpurin and carbon dioxide. Two other anthracene derivatives also occur in madder, both probably as decomposition products of pseudo-purpurin, munjistin,  $C_{15}II_8O_6$ , and xanthopurpurin,  $C_{14}H_8O_4$  (the latter of which is isomeric with alizarin).

The importance of madder and madder preparations has almost entirely disappeared with the development of the artificial alizarin manufacture. The colors obtainable from alizarin, isopurpurin or anthrapurpurin, and flavopurpurin, which are the products of the synthetical methods, have almost entirely replaced those formerly obtained from madder.

4. Safflower (syn. Safflor, Fleurs de Carthame) consists of the dried flowers of the Carthamus tinctorius, a plant first grown in Egypt and the East Indies, but now grown in Asia Minor, Spain, Alsace, Austria, and Central Germany. The flowers are of a deep reddish-orange color, and contain, besides a yellow coloring matter of no technical value, carthamin, or carthamic acid, C<sub>14</sub>H<sub>16</sub>O<sub>7</sub>, a red dye of considerable importance for silk- and cotton-dyeing. It forms from .3 to .6 per cent. of the weight of the flowers. "Safflower carmine" is a solution of the cai thamin in soda, and "plate carthamine" is a pure preparation of the cai thamin in soda, and "plate carthamine" is a pure preparation of the most important commercial varieties of safflower are the Egyptian, which is the richest in dye-color, the East Indian, the Spanish, and the German. Safflower comes from Spain and France, the production hav-

ing amounted in recent years to 400,000 pounds. However, it is now almost entirely displaced from use as a dye by the artificial dyes.

5. Orseille, or Archil (syn. Orseille, Persio, Cudbear).—The various species of lichens, as Rocella tinctoria and Rocella fuciformis from Angola, Zanzibar, Ceylon, and Mozambique, as well as from the Azores and South American coast, contain a mixture of phenols, phenol-ethers, and phenol-acids, such as orcin (or orcinol), erythric, orcellinic and lecanoric (or diorcellinic) acids. These by the action of air and ammonia yield orcëin, contained in the orseille (archil) extract as a red dye, and on drying the extract the cud-bear or persio as a reddish-violet powder.

Archil extract occurs in commerce in two forms, paste and liquor. The solid matter consists mainly of the impure orcëin in combination with ammonia. Its preparation will be referred to later. Cudbear (or Persio) differs mainly from the orseille extract in being free from all excess of ammonia and moisture and in being reduced to a fine powder. An illustration of the orseille-yielding lichens is given in Fig. 112 (see page 489) in the lower left-hand figure.

6. Cochineal (syn. Cochenille) is the dried female insect Coccus Cacti, which lives and grows on the plants of the Cactus family, especially the "nopal," or Cactus opuntia. The nopal-plant is indigenous to Mexico, but is also cultivated largely in Central America, the Canary Islands, the Island of Teneriffe, Algeria, and the East Indies.

The commercial varieties of cochineal are known as the silvery-gray and the black cochineal. These varieties are apparently produced according to the method adopted for killing the insects when they are swept off the leaves of the nopal-plant. If killed by immersion in hot water or by steam they lose the whitish dust with which they are covered and constitute the black variety (zaccatila); if killed by dry heat in ovens this dust remains and they yield the silvery-gray variety (blanco). This latter is considered the better, and is sometimes simulated by dusting the black variety with powdered tale, gypsum, barytes, or stearic acid. The natural gray powder is a variety of wax known as coccerin.

The coloring matter of the cochineal is carminic acid,  $C_{17}H_{18}O_{10}$ , and may amount to fifteen per cent. of the weight of the dried cochineal, although Liebermann states that the average is from nine to ten per cent. Carminic acid is a purple substance soluble in water and alcohol, but only slightly so in ether. Chlorine readily destroys the carminic acid and nascent hydrogen reduces it to a leuco body, which again becomes red on exposure to the air. Chemically it is a glucoside, being capable of decomposition into carmine-red,  $C_{11}H_{12}O_{7}$ , and a sugar,  $C_{n}H_{10}O_{n}$ .

Carminic acid dissolves in caustic alkalies with a beautiful red color, forms purple precipitates with barium, lime, lead, and copper, and a fine red lake with alumina. A decoction of cochineal behaves with reagents somewhat differently from a solution of the pure carminic acid owing to the presence of phosphates, tyrosine, etc. The addition of alum or stannic chloride to it yields the fine red pigment known as "cochineal

- carmine." This as well as other preparations from cochineal will be referred to again under products. (See p. 507.)
- 7. Kermes (syn. Kermés, Alkermes) is a corresponding substance to cochineal, and consists of the dried female insects Coccus Ilicis, which burrow under the epidermis of the leaves or young shoots of the kermes oak (Quercus coccifera), growing in the south of France, Spain, and Algeria. The coloring matter of the kermes insect has not been sufficiently investigated; it is said to be identical with that of cochineal. It is not used any longer in dyeing.
- 8. Lac dye (syn. Fürberlack) is the product of the Coccus Lacca, an East Indian insect which lives on the branches of the fig and other trees. The female insects exude a resinous substance which encloses them and attaches them to the twig. This constitutes the "stick-lac" (see p. 108), which contains about ten per cent. of coloring matter. This latter may be obtained by treating the stick-lac with carbonate of soda. The coloring matter of lac dye has been studied by Schmidt, who terms it laccainic acid,  $C_{10}H_{12}O_8$ , and found it to be very similar to carminic acid in most of its reactions. Many writers consider the two to be identical.

### B. YELLOW DYES.

- 1. Old Fustic (syn. Gelbholz, Bois jaune) is the trunk wood of Morus tinctoria, indigenous to the West Indies and South America. It is also yielded by the Maclura tinctoria and Broussonetia tinctoria. The wood is hard and compact and has a pale citron-yellow color. It contains two coloring principles, morin, or moric acid,  $C_{15}H_{10}O_7$ , which occurs in the wood combined with lime, and maclurin, or moritannic acid,  $C_{13}H_{10}O_6$ , both of which are yellow dyes and are contained in the commercial extract.
- 2. Young Fustic (syn. Fisetholz, Bois de fustct) is the bark-free wood of the Rhus cotinus, a variety of sumach growing in the Levant, Spain, Hungary, Tyrol, and Italy. The coloring matter is stated by Schmidt to occur as a soluble compound of fustin and tannic acid. This fustin is a glucoside, and is decomposed by dilute sulphuric acid into fisetin,  $C_{15}H_{10}O_6$ , and isodulcite. A decoction of young fustic gives a fine orange color with alkalies and bright orange precipitates with lime and baryta-water, stannous chloride and lead acetate. It also gives a fine orange color with alumina mordants. Is largely used in the dyeing of glove-leathers.
- 3. Quercitron is the crushed or rasped bark of the Quercus nigra or Quercus tinctoria, indigenous to North America, and grown also in Germany and France. It forms a brownish-yellow powder, from which an extract is also made. The coloring principle is quercitrin,  $C_{21}H_{22}O_{12}$ , a glucoside, which is decomposed by dilute sulphuric acid into quercetin,  $C_{15}H_{10}O_7$ , and isodulcite. Besides quercitin, the bark contains quercitannic acid,  $C_{17}H_{10}O_6$ . Quercitin is difficultly soluble in water, but easily soluble in alkalies with golden-yellow color. "Flavine" is the commercial name of a preparation of quercitron obtained by acting upon the bark first with alkalies and treating this extract with sulphuric

acid; it is a varying mixture of quercitrin and isodulcite, having some sixteen times the coloring power of the bark.

Flavine and quereitron bark are used chiefly for dyeing cottons and woollens with tin mordants.

4. Persian Berries, or Avignon Berries (syn. Gelbbeeren, Graines jaunes), are the dried fruit of different buckthorn (Rhamnus) species. The different commercial varieties are the Persian (from Rhamnus amygdalinus and Rhamnus-cleoidus), coming from Aleppo and Smyrna, regarded as the richest in dye color and the best in use, the French, or Avignon (from Rhamnus infectoria and Rhamnus saxatilis), the Levantine, or Turkish (from Rhamnus infectoria and Rhamnus saxatilis), and the Spanish (from Rhamnus saxatilis) and the Hungarian (from Rhamnus amygdalinus, etc.).

The coloring matter of the Persian berries is called by Liebermann xanthorhamnin, or chrysorhamnin, and is a glucoside, yielding under the influence of dilute acids rhamnetin,  $C_{16}H_{12}O_7$  (or methyl-quercetin,  $C_{15}H_0O_7CH_3$ ), and isodulcite. Persian berries are used for yellows on wool and cotton with alumina or tin mordants.

- 5. Weld (syn. Wau, Gelbkraut, Gaude) consists of the leaves and other parts of the Reseda luteola, a variety of mignonette. It is cultivated in almost all parts of Europe, notably in the south of France, Germany, and England. The coloring matter is known as luteolin,  $C_{15}H_{10}O_6$ , and forms yellow crystals of silky lustre, insoluble in water, soluble in alcohol. It dissolves in alkalies with deep yellow color. It is used especially in silk-dyeing.
- 6. Annatto (syn. Orlean, or Roucou) is prepared from the fleshy pulp of the seed-shells of the Bixa orellana, indigenous to the West Indies and South America, but cultivated also in the East Indies. The commercial annatto forms a soft reddish-yellow paste of buttery consistency, or sometimes it is dried in hard cakes. It contains two coloring matters, bixin, C<sub>28</sub>H<sub>34</sub>O<sub>5</sub>, and orellin, the former of which—the more important—is a red dye and the latter a yellow. The bixin dissolves in alkalies with yellow color. It is but little used in silk-dyeing. Orellin is as yet only slightly studied, and is considered by some to be simply an oxidation product of bixin. By far the largest amount of annatto is used not in dyeing but in coloring butter and cheese. (See p. 295.)
- 7. Turmeric (syn. Gelbwurz, Curcuma) is the tuber of the Curcuma tinctoria and Curcuma rotunda. The roots are usually grayish-yellow on the exterior but deep yellow in the interior. The plant is indigenous to Central Asia. The varieties of it are the Chinese, Java, and Bengal, of which the latter is considered the best. The coloring principle is curcumin,  $C_{21}H_{20}O_6$ , which acts like a weak acid. The pure color is bright orange-red, but it dissolves in alkalies with a red-brown color. It is seldom used as a dye, and then only for shading blacks on silk.
  - C. Blue Dyes.
- 1. Indigo (syn. Indig-blau, Indigo).—This is by far the most important of all the vegetable dyes. It has been known from very early times in the East, but was not introduced into Europe until the six-

teenth century, where its use was at first prohibited because of the general culture of the woad, and indeed it was only in 1737 that its employment was legally permitted in France. However, in time it displaced the woad almost entirely, so that the latter is used now only in a few special cases.

The indigo-plant is an *Indigofera*, the more important varieties of which are the *Indigofera tinctoria*, cultivated in India, particularly in Bengal, Coromandel, Madras, Java, and Manila; the *Indigofera Anil*, cultivated in Guatemala, Caracas, Brazil, and the Antilles; the *Indigofera Argentea*, cultivated in Egypt, Senegal, and the Isle of France. Of lesser importance are the *Indigofera disperma* and the *Indigofera pseudotinctoria*, both cultivated in the East Indies. The *Indigofera tinctoria* is shown in Fig. 112 (see p. 489) to the left of the illustration above. The indigo dye does not exist as such in the plant but as the result of fermentation, whereby the naturally occurring *indican*, a glucoside, is decomposed, most probably according to the reaction:

$$2C_{_{26}}H_{_{31}}NO_{_{17}} + 4H_{_2}O = C_{_{16}}H_{_{10}}N_{_2}O_{_2} + 6C_{_0}H_{_{10}}O_{_6}.$$
 Indigan. Indigo-blue. Indiglucin.

The plants are cut at two or three different periods in the year when they have just come into bloom. They are at once packed into bundles and put into the soaking-vats covered with water. A fermentation here ensues, which is completed in from ten to eighteen hours, according to the temperature of the air and the ripeness of the plants. When the supernatant liquid has taken a yellowish-green color and has a pleasant sweetish taste, the fermentation is stopped and the liquid is run off into vats placed at a lower level. Here it is beaten vigorously with sticks or paddles for from one and a half to three hours by men who enter the vats for the purpose. The liquid is changed by this treatment to a deep-blue color and becomes covered with froth of like color. the men leave the vat to rest, the separated indigo rapidly settles, and in some two to three hours the supernatant liquid can be run off from stopcocks placed in the side of the vat at levels above the indigo precipitate. Milk of lime is often added to hasten the settling of the separated indigo, and more recently dilute ammonia has been used. The addition of this latter reagent is said to increase the yield of indigo and to improve its quality, as it contains less indigo-brown and resinous impurities. The thin paste of indigo and water is then drawn off, boiled to prevent subsequent fermentation, and strained through a sheet. It is then put into square press-boxes lined with cloth and provided with holes in the sides and bottom for thorough drainage of the indigo. Pressure is then applied, gentle at first but stronger as the indigo hardens and acquires a firmer consistency. The mass is then cut into cubical blocks, which are stamped with the name of the factory and put on shelves in the drying-house to slowly dry out, great care being taken to avoid drafts of air, which might cause the cakes to crack in drying. Three hundred kilos, of indigo-plants yield an average of one kilo. of indigo. The commercial product contains from twenty to eighty per cent of the indige him forcer ging should

and with this two other coloring matters, indigo-brown and indigo-red, besides indigo-gluten, moisture, and a variable amount of mineral matter.

The commercial varieties of indigo are, first, the Asiatic, of which the Bengal indigo is the best, followed by the Java, Madras, Coromandel, and Manila varieties; second, the American, of which the Guatemala is the best, followed by the Caracas and the Brazilian varieties; and, third, the African, including the Egyptian, Senegal, and Isle de France varieties.

Indigo-blue is insoluble in water, alcohol, ether, dilute acids, and alkalies, soluble in fuming sulphuric acid, aniline, nitrobenzene, chloroform, and glacial acetic acid. It may be sublimed by heat, although with partial decomposition when the sublimation is carried out at ordinary atmospheric pressure. By the action of alkaline reducing agents it is changed to indigo-white,  $C_{10}H_{12}N_2O_2$ , and dissolved. Upon this reaction and the subsequent change of the indigo-white, when deposited upon the textile fibre, by atmospheric oxidation back again into indigoblue, is based the use of indigo in vat-dyeing. (See p. 536.) Indigo has been extensively used for cotton and wool dyeing, but is being largely replaced by the artificial indigo.

2. Wood (syn. Waid, Pastel).—The leaves of the Isatis tinctoria and Isatis lusitanica moistened, slightly fermented, and then compacted and dried into balls constitute the woad of commerce and furnish an additional source of indigo. As before stated, the use of the woad for dyeing antedated the use of the indigo-plant, and the cultivators of the woad, particularly in Central Germany, long fought against the introduction of the richer tropical indigo-yielding material, but in vain. The woad-culture is still carried on in different parts of Europe, particularly in France and Germany, but in small degree compared with its former development. The woad contains only .3 per cent. of indigo reckoned on the weight of the fresh leaves, or as it is often calculated, one hundred kilos. of woad have the same coloring power as two kilos. of indigo. The woad balls improve in quality by keeping for some years, the best variety coming from the south of France under the name of Pastel. The woad is rarely used by itself in dyeing operations, but along with indigo as a means of inciting the fermentation in the "woad-vat" process of dyeing.

A few other plants, such as *Polygonum tinctorium*, indigenous to China, and *Eupatorium tinctorium*, indigenous to Brazil, have been found to contain indigo, and have been used locally for blue-dyeing.

3. Logwood (syn. Blauholz, Bois de Campêche).—This is the heartwood, freed from bark and sap-wood, of the Hæmatoxylon Campechianum, a tree indigenous to Campeachy Bay, Central America, but grown now in various parts of Central and South America and the West Indies. The commercial varieties are the Campeachy, Yucatan, Laguna, Honduras, Jamaica, Haiti, St. Domingo, Monte Christo, Fort Liberté, and Guadeloupe logwoods. The principal sources now are Jamaica, Haiti, and St. Domingo.

Of the the first commands the highest price on account of the

d

large yield of coloring matter obtainable from it and the readiness with which it "bronzes" when submitted to the "curing" process. The wood comes in logs or sticks of smaller size, and is then chipped or rasped by the makers of extracts, who sell it in the chipped or rasped condition as well as in the form of prepared extract. The wood has a dark-red color on the exterior but is yellowish-red in the interior, has a weak odor of violets and a peculiar sweetish but astringent taste. On moistening the wood or chips with ammonia it takes a dark-violet color. Logwood contains some nine to twelve per cent. of the chromogen, hamatoxylin, C16H14O6, which is present in the wood partly in the free state but mainly as glucoside. It forms colorless prismatic crystals difficultly soluble in water, easily soluble in alcohol and ether. From the hæmatoxylin by oxidation in the presence of alkalies, and particularly ammonia, is produced hæmatëin, C<sub>16</sub>H<sub>12</sub>O<sub>5</sub>, the true dye-color. This forms small crystals or crystalline scales of dark-red color and greenish metallic lustre, which show plainly upon the wood, especially after the fermentation or curing. It is difficultly soluble in water, alcohol, and ether. Hæmatëin forms a crystalline compound with ammonia,  $C_{16}H_{11}(NH_4)O_6 + H_2O$ , which, however, is decomposed by acids or by heating to 130° C., leaving pure hæmatëin. Zinc and sulphuric acid readily reduce the hæmatëin to hæmatoxylin again. Logwood is used on an extended scale in dyeing wool, silk, cotton, and leather. It is used for deep blues, blacks, and jointly with other coloring matters for composite shades of color.

4. Litmus (syn. Lakmus, Tournesol).—This is a dyestuff very similar in character to orseille and persio (see p. 491), and also derived from the class of lichens. For its preparation the same lichens may be used, although at present the different species of Lecanora serve as the chief material, such as Lecanora orcina, L. dealbata, L. parella, which occur in the French Pyrenees, and the Lecanora tartarea, occurring in Iceland and Scandinavia. The lichens are allowed to ferment after the addition of stale urine or ammonia and carbonate of potash. When the mass has assumed a deep-blue color, chalk or gypsum is added, and it is shaped into small cubes and dried. The coloring matter is azolitmin,  $C_7H_7NO_4$ , which differs by one atom of oxygen only from the orcëin of orseille extract,  $C_7H_7NO_3$ . It acts like a weak acid, the salts of which are blue in color (the potassium compound existing in the commercial litmus), and which when set free by acids is reddish in color.

### D. GREEN DYES.

We have practically nothing here that has assumed practical value as yet. The only ones needing mention at all are:

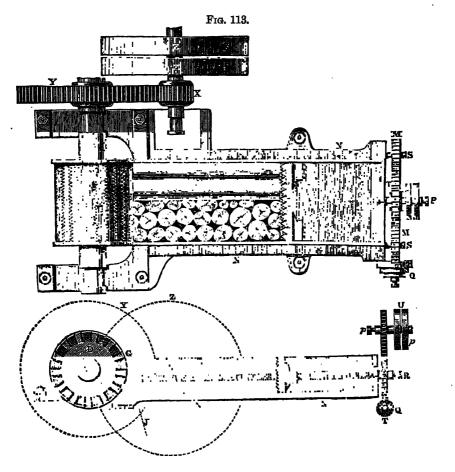
1. Chlorophyll.—This is the green coloring matter of fresh vegetation, and is abundantly present in nature, but it has not been found possible hitherto to isolate it in a pure state adapted for use. Schütz has, however, separated it from the yellow coloring matter accompanying it, xanthophyll. It is stated that chlorophyll forms a beautiful green color with zine as mordant which is adapted for dyeing, but it has not as yet been used in practice.

- 2. Lokao, or Chinese Green, is a green pulverulent deposit from the decoction of the bark of Rhamnus chlorophorus and Rhamnus utilis, both indigenous to China. Kayser, who has investigated the lokao, states that the coloring matter is lokaonic acid, C<sub>42</sub>H<sub>48</sub>O<sub>27</sub>, which is combined in the commercial preparation as the alumina lake. This lokaonic acid is decomposed by acids into lokanic acid, C<sub>38</sub>H<sub>38</sub>O<sub>21</sub>, and lokaose, an inactive sugar. Lokao has been used for cotton- and silk-dyeing, but is practically displaced by the cheaper artificial colors.
  - E. Brown Dyes.
- 1. Catechu (or Cutch).—This has already been spoken of as one of the raw materials of the tanning industry. (See p. 359.) It finds, however, an equally extended use in dyeing as an adjective color. The explanation of this is that catechu contains two principles, catechin,  $C_{21}H_{20}O_0 + 5H_2O$ , a yellow dye forming brown precipitates with copper, alumina, and tin mordants, and catechutannic acid,  $C_{12}H_{12}O_5$ . The former is present in amount from twenty to thirty per cent., the latter, however, from forty-eight to fifty-two per cent. The best variety of catechu is the Pegu catechu, and after this the Bombay and the Bengal catechu. Catechu is extensively used in both cotton- and silk-dyeing for browns and for composite shades.
- 2. Kino is a natural dyestuff very similar to catechu and comes from a variety of sources, as Butea frondosa and Butea superba, yielding the Bengal kino; Pterocarpus erinaceus, yielding the West African kino; Eucalyptus corymbosa and other Eucalyptus species, yielding the Australian kino. The important principles are kinöin,  $C_{14}H_{12}O_6$ , and its anhydride, kino-red,  $C_{28}H_{22}O_{11}$ . It is used like catechu for dyeing.

### II. Processes of Treatment.

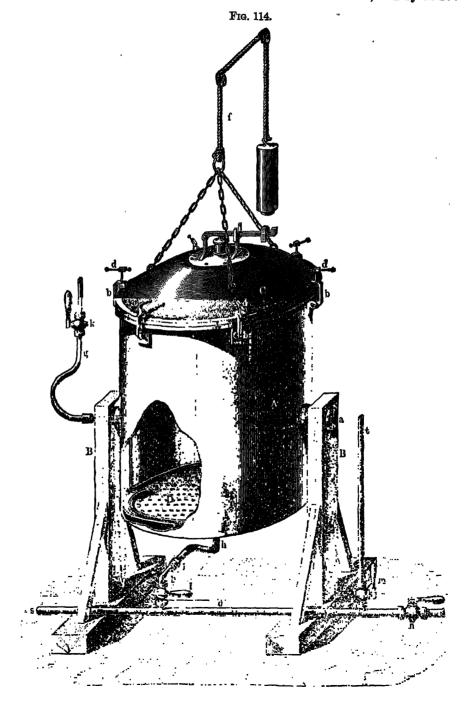
1. Cutting of Dye-woods.—Whether the dye-woods are to be used for the manufacture of extracts or used as wood by the dyer, they must be reduced to powder or cut into chips of small size. This process varies with different manufacturers. In America, it is usually one of cutting with powerful knives, in which whole logs are brought with their ends against rapidly-revolving cylinders, on the circumference of which are heavy steel knives, which cut off flat chips directly across the grain about one-eighth inch in thickness. This method is a very rapid one, as but little previous splitting of the logs is necessary. In Europe, where labor is cheaper, the logs are frequently sawed and split into billets about two feet long, and two to three inches in thickness, and these are then brought by hand diagonally against toothed knives on a rapidly-revolving cylinder, by which means the wood is torn or rasped into a much finer condition, or these billets are put into a machine which presses them in this way against the revolving knives. Such a machine of German design is shown in Fig. 113, where a rotating drum, D, carrying on its circumference a series of knife-blades, is continuously cutting the billets of wood which are pressed against it.

2. Fermentation or Curing of Dye-woods.—As has already been stated in several cases, the dye-woods in the fresh condition contain not the finished dye-color, but a chromogen capable of passing into the former under the influence of oxidizing or other agents. Notably is this the case with logwood, and the chips or rasped wood are therefore submitted to a curing treatment by moistening them with water and expos-



ing them to the air in heaps some three feet in depth for from four to six weeks. The chips heat up, and the pile must then be turned with shovels to regulate the temperature and allow contact with the air. More water is then added, and the process continued until the chips assume a rich reddish-brown color or become coated with a bronze powder (hæmatëin). Various chemicals have been suggested to hasten the operation, such as ammonium carbonate and chloride, stale urine, sodium carbonate, potassium nitrate, chalk, and glue. None of these are known certainly to be of benefit. The alkalies give the chips a fine red color at first, but unless great care is taken they cause them to become black from

over-oxidation before the action can be checked. Glue has been use because it is said to combine with the tannin of the wood, and by remov



ing it to open up the pores of the wood to the oxidizing influence and so facilitate the curing. But the existence of tannin in logwood has not been at all certainly established.

Curing is of value to the dyer because it enables him to rapidly obtain the color from the chips and gives him a liquor containing a more highly oxidized coloring matter, which "goes on" the goods more rapidly. It must be remembered, however, that curing the chips enables the manufacturer to sell twenty to thirty per cent. of water with them, while uncured chips contain only ten to fifteen per cent. of moisture.

When the chipped logwood is intended for the manufacture of extract it is usually conveyed directly to the extractors without curing, which is, no doubt, the better procedure, since all oxidation in the first part of the process is objectionable.

3. Manufacture of Dye-wood Extracts.—As dye-woods contain generally only a tenth or less of their weight of dye-color, it becomes a matter of great economy in transportation and storage to prepare from them extracts, either as concentrated liquids or solids representing the active coloring principle. This is done by manufacturers who make a specialty of this extracting, and apply to it the best designed and most improved machinery.

The operation may be divided into two stages,—the extraction and the concentration. For extraction a rasped wood such as is made in France has many advantages over the chipped, since it yields its coloring to a smaller quantity of water and at a lower temperature than the The extraction consists in heating the wood with water under various conditions and then drawing off the liquor into tanks for settling or treatment. The conditions refer to the kind of vessels, the amount and quality of the water, and the temperature. Many European manufacturers use open wooden vessels for extractors, so that the temperature does not get above 100° C. As this method was first used in France, it is known as the French process. The use of closed extractors, however, allows of increase in the pressure, and this within limits much facilitates the perfect extraction. A closed extractor of German design, in which a pressure not exceeding two atmospheres is used, is shown in Fig. 114. (See preceding page.) It will be seen that the vessel, A, is provided with a false bottom, D, to allow of the draining off the extract liquor, a perforated steam-pipe, g, to rapidly bring up the contents of the extractor to the required temperature, and a drainagepipe, h, to draw off the thin extraction liquors.

In America closed copper or iron vessels are used, arranged in battery form very much like the diffusion apparatus now used in the extraction of sugar. One cell of such an extraction battery is shown in Fig. 115. This method allows of continuous working, as one cell of the series can be emptied of exhausted dye-wood and loaded with fresh chips while the extraction liquors are passing successively through the other cells of the battery and acquiring the maximum strength. The temperature or pressure varies with different manufacturers, but most writers on the subject agree that a pressure not exceeding fifteen to

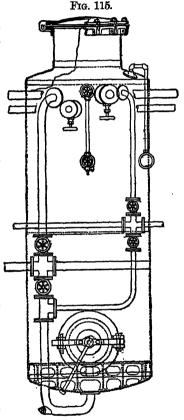
be used. An increase in the yield, coloring value of the

increase in the pressure is always attended with an increase in the yield, and after a certain point with a decrease in the coloring value of the resulting extract. When the liquors from the extractors are run into large tanks and allowed to cool much wood-fibre and some resinous matter separates. The clear liquor is then drawn into the evaporators, which in this country almost invariably consist of vacuum-pans, but in Europe

often consist of open pans or vessels in which heated disks revolve so as to favor the evaporation. While the liquor is still thin, double- or triple-effect pans are used, and of recent years the Yaryan evaporators (see Fig. 38, p. 144) have been applied with great success to the evaporation of dye-wood extracts. As the liquors become thicker the concentration is continued vacuum-pans more analogous to strike-pans of the sugar refinery. Such a vacuum-pan designed for use in the manufacture of dye-wood extracts is shown in Fig. 116. When the gravity of the liquid becomes 42° or 51° Tw., it is drawn off into barrels for shipment, or if the solid extract is desired the concentration is continued in a vacuum-pan.

twenty pounds excess over atmospheric .....

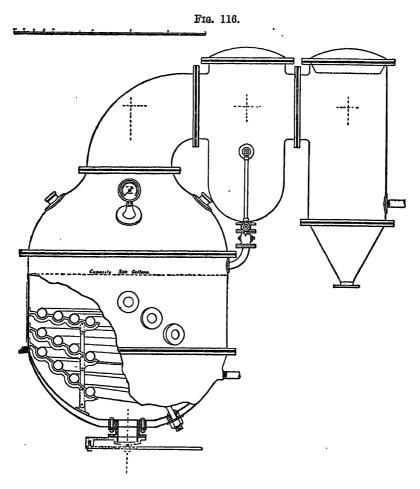
Various methods of treatment have been suggested at different stages of the process with a view of improving the extract, but it is an open question whether anything better than pure water has yet been used. The addition of solutions of glue and of different salts to the wood before extraction has been frequently recommended. Chalk suspended in water and dilute limewater have also been recommended to



be similarly used. Such processes could only result in an over-oxidized product. Borax has also been used, but without notable advantage in the case of logwood, although it serves very well in the case of the redwoods. The use of chlorine, hypochlorites, and chlorates has been patented in connection with logwood extract for addition either to the wood or the liquor after extraction, but it is doubtful if any of these are used on a large scale at the present time. That these substances and many others develop the color of logwood there can be no question, but to be of value to the dyer that development must take place in the presence of the goods.

The yield of logwood extract by the American process of manufac-

ture is said by Soxhlet\* to be twenty or twenty-one per cent. of solid extract, while that by the French process is sixteen and a half per cent. The latter is superior in quality, and is therefore almost invariably reduced by the addition of such substances as molasses, glucose, and extract of chestnut. In America, in addition to the above, extract of



hemlock and extract of quercitron (after the removal of the flavine) are considerably used to adulterate logwood extract.

4. MISCELLANEOUS PROCESSES.—(a) Preparation of Guarancine and Madder Flowers.—For the preparation of guarancine, the pulverized madder-root is warmed gently with dilute sulphuric acid (one part acid and two parts water) for some time, whereby the glucosides of the madder are decomposed. The sugary liquid is drained off and the resi-

<sup>\*</sup> Textile Colorist, xiii, p. 125.

due heated with concentrated sulphuric acid, which decomposes the woody fibre and other organic substances present and decomposes any lime compounds that may have been in the madder. The whole mixture is now thrown into water, the precipitate collected, washed, and dried. The guarancine now contains the alizarin and purpurin in uncombined form. The yield is from thirty-four to thirty-seven per cent. For the preparation of "madder flowers" the powdered madder is set to ferment with warm water to which a little dilute sulphuric acid had been added. After some days, the liquid is filtered and the residue washed, pressed, and dried. The flowers of madder can be used more readily than crude madder in dyeing at low temperatures, and give finer and purer violets.

(b) Preparation of Ammoniacal Cochineal and Carmine.—Five parts of powdered cochineal are mixed with fifteen parts of ammonia-water, and the mixture is allowed to stand in a warm place with frequent stirring for some four weeks. Some two parts of alumina are then added, and the mixture carefully evaporated in a porcelain dish until the odor of ammonia has disappeared. The preparation so obtained, known as ammoniacal cochineal, yields its color more readily than cochineal and produces brighter shades of color.

Cochineal-carmine is a brilliant red pigment prepared from decoction of cochineal by the action of alum under certain conditions. details of its preparation vary and are kept by different manufacturers as trade secrets. The following process has been published: \* Five hundred grammes of finely-powdered cochineal are boiled for one-quarter of an hour with thirty times the weight of distilled water, thirty grammes of acid tartrate of potassium added, boiled for ten minutes longer, fifteen grammes of alum added and boiled for two minutes longer. The clear liquid is allowed to stand in shallow glass vessels, when the carmine separates in a very fine state. It is washed with water and dried in the shade. Or, by another process, t one pound of cochineal and one-half ounce of potassium carbonate are boiled with seven gallons of water for fifteen minutes. The heat having been withdrawn, one ounce of powdered alum is added, and the liquid stirred and allowed to settle. The clear liquid is decanted, one-half ounce of isinglass added, and heat applied until a coagulum forms, when the liquid is briskly stirred and allowed to settle.

(c) Preparation of Flavine.—As stated before (see p. 492), flavine is a preparation containing the coloring matter of the quereitron bark in purer and more concentrated form. The method for its preparation is not generally known, although it is found to contain quercetin as well as quereitrin, and frequently the former in larger amount.

A procedure that has been published ! is the following: Two hun-

<sup>\*</sup> Schützenberger, Die Farbstoffe, ii, p. 338.

<sup>+</sup> Allen, Commercial Organic Analysis, 2d ed., iii, p. 367.

<sup>‡</sup> Gerb- und Farbstoffe-Extracte, Mierzinski, p. 208.

dred and fifty kilos. of the powdered quercitron are boiled for fifteen minutes with fifteen kilos. of crystallized soda and two hundred kilos. of water, there is then added to the liquid sixty-one kilos. of sulphuric acid of 66° B., and the boiling continued for three-quarters of an hour longer, when the whole is allowed to cool and settle, the liquid poured off, and the separated color drained and dried.

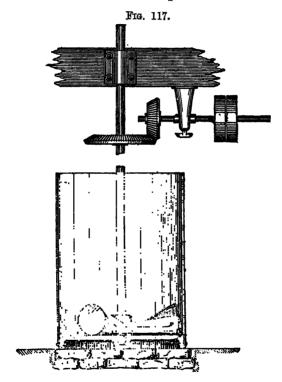
(d) Preparation of Indigo-carmine, Soluble Indigo, etc.-It was stated in an earlier section (see p. 495) that indigo-blue was soluble in strong sulphuric acid. The solubility depends, however, upon the chemical action of the acid, whereby sulphonic acids of indigo are Two such acids, indigo-monosulphonic acid (sulpho-purpuric acid),  $C_{16}H_0(HSO_3)N_2O_2$ , and indigo-disulphonic acid (sulphindigotic acid),  $C_{16}H_8(HSO_3)_2N_2O_2$ , are formed. Of these, the first is insoluble in water or dilute acids, while the second is soluble with deep-blue color. Both are formed together in practice when indigo is dissolved in strong sulphuric acid, although if not more than four parts of sulphuric acid to one of indigo be used and too prolonged heating be avoided, the monosulphonic acid will be formed predominantly, while if some fifteen parts of ordinary concentrated sulphuric acid or seven parts of fuming sulphuric acid be taken to one of indigo and the heating be continued, the disulphonic acid will be the sole product. After treatment with the acid the dissolved mass of indigo is allowed to cool down and then strained to remove any lumps that may have escaped grinding; salt is thrown in, which precipitates the indigo-sulphonic acids, which are removed by filtration through felt. For finer grades of "indigo extract "the precipitate is redissolved in water and reprecipitated with salt several times, each precipitation removing a greater quantity of the objectionable green coloring-matter. Whatever be the process or proportion of acid used, the indigo must be very finely ground. This is done in indigo-mills, which are of various forms, known as "ballmills," in which rotating cannon-balls gradually grind the color, as "cylinder-mills," in which heavy iron rolls accomplish the same work. and other forms. An illustration of such an indigo-mill with conical rolls, taken from a form in current use, is shown in Fig. 117. Indigo grinding for "extract" making is of little importance since the introduction of dry synthetic indigo. The direct use for dveing of the product obtained by the action of sulphuric acid upon indigo is no longer The preparation and sale by the color manufacturers of pure preparations, known as Indigo Extract, Soluble Indigo, or Indigocarmine, has replaced them. The sodium salt of the monosulphonic acid constitutes "indigo-purple" or "red indigo-carmine," the sodium salt of the disulphonic acid the true "indigo-carmine," which comes into commerce in paste form under that name or as a dry powder known as " Indigotin."

This indigo-disulphonic acid fixes itself on the animal fibre like other acid colors, and is dyed in an acid bath containing sulphuric acid.

## III. Products.

1. From Red Dyestuffs.—(a) Brazil-wood Extracts are made by the diffusion process, three varieties coming into commerce,—a liquid extract of 20° B., a liquid one of 30° B., and a solid one. One kilo. of the dry extract corresponds on the average to twelve kilos. of the wood. Brasilin is also manufactured on a large scale almost pure by Geigy, of Basle.

This brasilin often separates in the form of a crystalline crust on the surface of the commercial extract liquors. These crusts contain the



brasilin mixed with the lime compound of the same. If this crude product is boiled with very dilute alcohol with the addition of zinc dust and hydrochloric acid, and the solution stood aside to crystallize, a very pure product is obtained.

Brasilin is relatively easily soluble in water, alcohol, and ether. In alkalies it is soluble with carmine-red color. Zinc dust will decolorize the solution, but on exposure to the air it speedily takes up the red color again. Acetate of lead precipitates a colorless crystalline compound which gradually turns red. Brasilëin bears the same relation to brasilin that hæmatëin bears to hæmatoxylin, and can be prepared by the oxidation of the alkaline solution of brasilin in the air.

Brazil-wood extracts are used in wool- and cotton-dyeing. With alumina mordants they produce shades resembling the alizarin lakes,

but inferior in character. On wool mordanted with bichromate of potash they produce a fine brown.

The insolubility of the coloring matters in sandal-wood prevents their being used in the form of extracts.

(b) Madder Preparations.—We have already referred to Guarancine and Flowers of Madder. Guaranceux is the name applied to the impure purpurin recovered from the sediment of the waste-liquors in madder-dyeing.

Pincoffin (Alizarine commerciale) is a preparation from guarancine, in which the purpurin has been decomposed by superheated steam, leaving the alizarin unchanged. It has twenty-five per cent. less coloring power than the guarancine, but gives finer violets than can be obtained with the former.

- (c) Safflower Preparations.—These are practically more or less pure preparations of carthamin, and the names Safflower Extract, Safflowercarmine, Safflower-red, and Plate-red refer to different concentrations of the carthamin solution. For the preparation of the pure safflower-red. the safflower-yellow must be removed by washing the crushed flowers with water until this runs off colorless. The residue is then treated with water and fifteen per cent. of its weight of crystallized soda salt. The solution is strained from the residue, filtered, and after acidulating with acetic or citric acid, cotton yarn is immersed in it to take up the color. The dved cotton is stripped of the color by a five per cent, soda solution. and from this solution the color is again precipitated by citric acid. It is now drained, and comes into commerce as a paste known as "Safflower Extract." The color must be kept in sealed flasks, protected from the light. This paste dried upon plates at a gentle heat yields the so-called "plate-red." It then forms a red powder with greenish reflex, almost insoluble in water and ether, but easily soluble in alcohol. It is also soluble in alkalies with yellowish-red color. The "safflower-carmine," on the other hand, is prepared from the extract paste by washing the insoluble color and dissolving it in alcohol, which is then left to slowly evaporate. For dyeing purposes the safflower-carmine is dissolved by addition of soda, and the bath is then made slightly acid with citric acid; or the soda-extraction liquors from the flowers, which have been washed with water, may be used directly, acidifying the bath as before. Safflower-red is fixed in a weak acid bath both upon the animal fibre and upon the unmordanted cotton. On silk it produces a fine rose-red color.
- (d) Orseille Preparations.—These come into commerce both as paste and liquor. The solid matter consists essentially of the impure orcëin in combination with ammonia. It is liable to be adulterated with the spent weeds from the manufacture of the orseille liquor or with other vegetable coloring matters. It is also at times adulterated with aniline dyes, such as magenta, acid magenta, and methyl violet. Various azo dyes, producing colors ranging from crimson to claret-red, are now sold as substitutes for the orseille extract, and, being cheaper, are used to adulterate it. These are known as "orchil extract," "orchil-red," "orselline," etc. They may be detected when so admixed by their

behavior with salt solution and basic acetate of lead. The liquid extract is usually brought to 25° B., and is frequently adulterated with logwood or Brazil-wood extract. Orseille Purple (French Purple) is a pure orseille dye, obtained by extraction of the lichens with a fifteen per cent. ammonia solution, precipitation with hydrochloric or sulphuric acid, and redissolving in ammonia. This solution is then left exposed to the air in shallow vessels until it becomes dark purplish-violet. The color is then precipitated by addition of sulphuric acid, washed, and dried. Orseille Carmine is a similar preparation, in which the ammoniacal solution, after exposure to the air until it becomes cherry-red, is heated with alum or calcium chloride. Cudbear, or Persio, as before stated, is a dry powder obtained by evaporation of the extract, or prepared direct from the lichens by the action of ammonia or urine and then evaporated to the condition of a powder. It is often adulterated with common salt and other mineral matters, and is liable to much the same organic impurities or adulterants as orseille.

(e) Cochincal Preparations.—Ammoniacal cochineal and cochinealcarmine have already been referred to. Ammoniacal Cochineal is distinguished from carminic acid by giving a purple precipitate (instead of scarlet) with oxymuriate of tin. The crimson, purple, and mauve colors it yields with mordants are not affected by acids so readily as those produced directly by cochineal. Ammoniacal cochineal is used in admixture with ordinary cochineal for producing the bluer shades of pink. Cochineal-carmine requires for its production a decoction of cochineal itself and not of carminic acid, the nitrogenized matters being essential to its formation. Liebermann,\* who has investigated carefully the nature of the cochineal coloring matter, found it to contain 3.7 per cent. of nitrogen, of which only .25 per cent. could be expelled by boiling with dilute alkali, the remainder existing apparently as protëids. He gives the following as the composition of the commercial sample of carmine examined by him: Water, seventeen per cent.; nitrogenous matter, twenty per cent.; ash, seven per cent.; coloring matter, fifty-six per cent.; wax, traces. Liebermann considers cochineal-carmine to be no ordinary compound of a coloring matter with alumina, but as an alumina-albuminate of the carmine coloring matter, comparable in some respects to the product from alizarin and alumina with "Turkey-red oil." Carmine forms red, porous, relatively light masses, which are easily rubbed up to a fine red powder. It is insoluble in water and alcohol, but readily soluble, when pure, in aqueous ammonia. Cochineal-carmine is liable to adulteration with starch, kaolin, vermilion, red-lead, chrome-red, etc. These admixtures may be detected by treating the sample with dilute ammonia, in which a pure sample should be completely and readily soluble.

M. Dechan † has published a series of analyses of commercial carmine, which are here given:

<sup>\*</sup> Ber. Chem. Ges., xviii, p. 1971.

	1,	2.	3.	4.	5.	6.	7.	8.	9.	10.
Moisture Soluble in Coloring matter ether. Alumina, lime, etc. Organic matter . Ash Vermilion	22.1 46.1 8.0 21.8 2.0	16.1 69.2 9.8 2.5 2.4	2.0 34.1 11.4 18.5 34.0	22.3 65.7 12.0 Trace.	20.2 60 8 9.0 9.8 0.2	23.5 69.5 7.0 Trace.	8.5 26.1 0.4 14.6 50.4	10.0 72.0 8.1 8.0 1.9	21.2 18.4 4.4 52.4 3.6	13.0 67.5 10.0 9.5 Trace.

Cochineal is not used in cotton-dyeing. In dyeing silk it has also been almost entirely superseded by aniline reds, and in wool-dyeing the azo colors have to a great extent replaced it. Two distinct shades of red are obtained with cochineal, according to the mordant used,—cochineal-crimson with cream of tartar and alum, and cochineal-scarlet with stannous chloride and cream of tartar or oxalic acid.

- 2. From Yellow Dyestuffs.—(a) Old Fustic Extracts.—Both a liquid extract of about 20° B. and a solid extract have been prepared. The latter forms large yellowish-brown blocks of a waxy lustre, which dissolve in water with yellow color. They are prepared from the wood by diffusion. The name morin has been given to a commercial product obtained by boiling the rasped wood with a two per cent. soda solution and evaporating the solution so obtained to a specific gravity of 1.041, when on cooling the morin and moritannic acid separate out.
- (b) Quercitron Extracts, etc.—Both liquid and solid extracts are used commercially. The former of 20° and 30° B. respectively, and the latter as a dark-brown mass of waxy lustre. The extracts contain, as a rule, mixtures of quercitrin and quercetin. Flavine has already been referred to. It is a preparation in which the quercitrin of the bark has been extracted, and in large part changed by subsequent treatment with sulphuric acid into quercetin, which is superior in coloring power. The tannic acid of the bark extract has also been removed and the lime salts, so that it gives much purer colors than the original extract. Flavine is largely used in connection with cochineal or lac-dye for producing scarlet. A quercitron extract to which stannite of soda or sulphate of zinc has been added is said to be used under the name of "Fustic Substitute." It can be told from genuine extract of fustic by the test with ferric chloride, which produces a brown precipitate, turning olive-green with fustic, but a greenish-black with quercitron extract.
- (c) Persian Berries.—A thick extract is prepared from Persian berries, soluble in water with yellow color shading into brown. The solution becomes clearer on addition of hydrochloric or nitric acids and deposits a dirty-yellow precipitate. Ammonia or caustic soda colors it a reddish-yellow, stannous chloride gives at once, and stannic chloride after the addition of carbonate of soda, a golden-yellow precipitate, iron salts a dark olive-green to greenish-black color.
- 3. From Blue Dyestuffs.—(a) Commercial Indigo occurs in lumps or fragments of a deep-blue color, usually showing a bronze or purplered streak when rubbed with any hard substance, or in the case of the better kinds with the friction of the thumb only. The fracture of indigo is dull and earthy, it sticks to the tongue, is odorless and tasteless. The

specific gravity varies from 1.324 to 1.455. Helen Cooley \* has given the following determinations of indigotin, ash, and specific gravity in a number of samples of commercial indigo:

Descr	IPTION.	Specific gravity.	Ash.	Indigotin.
Watson's best . Bengal red Oude Bengal blue Kurpah red		1.292 1.891 1.427 1.481	17.54 6.50 6.41 7.02 7.50 21.20 14.49	55.11 59.53 54.03 52.90 57.60 45.28 47.04

Indigo preparations have been referred to under processes (see p. 504), and it was then noted that the salts of the indigo-sulphonic acids constituted the several so-called indigo extracts. *Indigo-carmine* is the potassium or sodium sulphindigotate (C<sub>16</sub>H<sub>8</sub>(SO<sub>3</sub>K)<sub>2</sub>N<sub>2</sub>O<sub>2</sub>). It comes into commerce in both paste and solid form. It is soluble in one hundred and forty parts of cold water, readily soluble in dilute sulphuric acid. It dyes animal fibres direct, but with a much lighter shade than indigo, and is not at all so fast to light, while to vegetable fibres it shows no affinity. An analysis of the several grades of carmine-paste by Mierzinski † gave:

DESCRIPTION.	Water.	Indigo.	Salt.
Carmine I	85.0	4.96 10.02 12.04	5.7 4.8 13.9

Saxony Blue (Chemic Blue) is the free sulphindigotic acid, C16H N<sub>2</sub>O<sub>2</sub>(SO<sub>3</sub>H)<sub>2</sub>, and forms a deep-blue solution. It is prepared as in the making of indigo-carmine, except the acid is not saturated with alkali It was largely used in dyeing wool, but is not adapted for silk. Indigo purple is a reddish-violet powder, which mixed with varying amount of orseille can be used for dyeing wool directly without mordants. Fo its preparation, powdered indigo is covered with ordinary (not fuming sulphuric acid, and having been cooled is left for half an hour. In thi way is obtained a blue solution of sulphindigotic (indigo-disulphonic acid, which can be worked up into indigo-carmine and a violet powder This latter is the monosulphonic acid, which is washed first with wate and then with dilute soda solution until the washings are no longer acid then dried for use as above. A product of analogous composition, know as Boiley's Blue, is prepared by gradually adding one part of finely powdered indigo to ten or twenty parts of acid sodium sulphate, HN SO<sub>4</sub>, in a state of fusion. The product is dissolved in water, precip tated with common salt, and washed with brine. Boiley's blue is crystalline light-purplish mass, soluble in water with beautiful blu violet color. Its solution in strong boiling acetic acid deposits on coo

<sup>\*</sup> Amer. Journ. Anal. Chem., ii, p. 130. † Ganswindt, Fürberei, p. 150.

ing large prismatic crystals exhibiting a coppery reflection. It is insoluble in alcohol or ether, but readily soluble in hot water. The light transmitted by the solution is red. With barium and strontium salts it yields violet precipitates.

The fact that indigo had been obtained artificially by several different methods was mentioned under the artificial dye-colors. (See p. 465.) A synthesis of indigo-carmine has also been effected within recent years. The process, due to B. Heymann,\* is as follows: One part of phenyl-glycocoll (CoHr.NHCH2.COOH) is rubbed up with ten to twenty times its volume of clean sand (which simply acts in the way of reducing the temperature of the reaction), and slowly added to fuming sulphuric acid, with eighty per cent. anhydride strength, warmed to 20° to 25° C. Care is to be taken that the temperature does not thereby exceed 30° C. After the solution of the phenyl-glycocoll, which takes place with evolution of sulphurous oxide, concentrated sulphuric acid of 66° B. is added to remove the excess of anhydride. It is then diluted with ice and common salt added, when indigo-carmine (indigo-disulphonic acid) at once separates out. Experiments on dyeing with the new product show it to be better and purer than the commercial indigocarmine. Its identity was established in a number of ways. The yield amounts to sixty per cent. of the theoretical, but this may be improved by further study of the conditions of the reaction.

(b) From Logwood.—Logwood Extracts are prepared as liquids of 12°, 42°, and 51° Tw. (for equivalents of the Beaumé scale, see Appendix) and as a solid. This latter forms a dry black, lustrous and resin-like mass, which is quite brittle and easily powdered, taste sweetish astringent, and yields a reddish-brown solution. The specific gravity ranges from 1.45 to 1.51. The specific gravity is not a reliable indication of the strength of the fluid extract, as it is liable to be raised by the addition of salt, glucose, molasses, etc. The extracts are also sometimes adulterated with starch, dextrin, chestnut-bark extract, hemlock extract, etc. The following table by Brühl † gives the yields of extracts ob-

DESCRIPTION OF WOOD.	Yield of extract	Soluble in ether.	Soluble in absolute alcohol.	Residue.
Yucatan Yucatan, E. J. Laguna St. Domingo St. Domingo O. Monte Christo, 1884 Monte Christo, 1887 Fort Liberté, 1886 Fort Liberté, 1887 Fort Liberté, 1887 Fort Liberté, 1887 Fort Liberté, 185-86 Fort Liberté, J. B., 1887 Jamaica Ja	21.00 14.02 19.80 18.75 14.00 20.33 16.00	60.12 58.34 51.87 44.95 43.81 . 82.00 84.72 41.89 50.00 59.72 59.24 43.20 43.20 43.05 52.99	87.46 88.51 47.95 53.47 50.32 60.82 54.10 54.11 47.92 85.17 34.81 50.50 50.71 80.12	2.42 8.15 0.68 1.58 5.87 7.68 11.18 4.00 2.08 5.21 5.95 6.80 6.24 16.89

<sup>\*</sup> Ber. Chem. Ges., xxiv, p. 1476.

<sup>†</sup> Textile Colorist, x, p. 148.

tained by himself from different woods and the percentage solubility of the resulting extracts in ether and alcohol. The portion dissolved be ether represents roughly the hæmatoxylin percentage, while that dissolved by absolute alcohol represents the hæmatëin and decompositio products of the hæmatoxylin.

Indiao Substitute (Noir imperial, or Kaiserschwarz).—Under thes names are known oxidized logwood extracts, made by boiling logwoo extract with copper, iron, or chromium salts with the addition of oxali They may be in liquid form, or pastes, or dry powders. Th preparations are almost insoluble in water, but completely soluble i acids with yellowish-brown color. A commercial preparation of thi class, known as "direct black," for cotton forms a brownish, visci liquid, composed of fifty per cent, water, forty-five per cent, of a sul stance soluble in alcohol and ether (hæmatoxylin and hæmatëin), an 3.5 per cent. of copper sulphate. Hæmatëin (Hématin) is a commer cial preparation of French origin, which claims to consist of nearly pur dyestuff. It forms a granular, reddish-brown powder, completely solubl in water, and dyes the same shades as those obtained from the wood Fifteen kilos. of hæmatëin are said to be equivalent to one hundre kilos, of the logwood. Hematine crystals is a solid logwood extract mad porous by the addition of nitrite of sodium just before solidifying.

- (c) Litmus, as has been said, is a mixture of the lichen dye of tha name with chalk or gypsum as inert material. It is made in differen numbered grades, containing different amounts of the mineral matter Litmus in the dry form has a violet-blue color, is quite friable, and dissolves in water and dilute alcohol, leaving a residue of chalk, gypsum alumina, silica, etc.
- 4. From Brown Dyes.—(a) Catechu has been described already in part under the raw materials of the tanning industry. (See p. 359. It is not unfrequently adulterated with starch, sand, clay, and blood Good catechu should yield at least half its weight to ether and should be entirely soluble in boiling water, the latter solution depositing catech on cooling. Catechu does not wholly dissolve in cold water unless in has been previously modified by age or exposure to damp. It shoul not yield more than five per cent. of ash. Prepared Catechu has been merely purified by mechanical means. For this purpose, the commercial catechu is fused on the water-bath, whereby sand, earth, and similar impurities settle out, and then it is strained to remove leaves, etc. The material so obtained is again melted on the water-bath, and the every one hundred parts of the catechu three-fourths per cent. of potas sium bichromate is added, when it is allowed to cool down again.

# IV. Analytical Tests and Methods.

1. For Dye-woods.—Here the question of adulteration does not com notably in play. The compact woods are not capable of much adulteration of any kind. When chipped or rasped, however, they may be adulterated quite considerably. The examination with the microscope of simple lens will often suffice to indicate the nature of this adulteration.

A special case of cheapening is that of the cured or fermented logwood chips, which, as has already been stated, may take up as the result of this fermentative process as much as thirty to forty per cent. of water. In this case a moisture determination will show the change, allowance being made for the fourteen per cent., which is the average moisture of the unfermented wood.

To determine the comparative dyeing value of different samples of woods, the only thoroughly reliable test is an actual dyeing test made with definite weights of the wood, thoroughly extracted, and using definite amounts of mordants upon the wool or other fibre used. test, as applied to logwood, for example, would be carried out as follows: Ten gramme portions of clean wool are separately mordanted for 11/2 hours at the boil with 3 per cent. of potassium bichromate and 21/2 per cent. of cream of tartar, washed, and dyed for 1 hour at the boil in the logwood bath, containing a definite amount of decoction or extract of each sample to be tested, afterwards washing and dyeing for the final comparison of shade. This method of logwood assay takes cognizance both of the actual and the potential coloring matter present (hæmatëin and hæmatoxylin), and is a more rational method of examination than any based on the color produced on cotton mordanted with alumina or The dye test in other cases must be made upon a normal prepared extract of known strength and purity, and the result compared with those obtained with a corresponding weight of the supposed adulterated sample.

2. For Dye-wood and other Extracts.—(a) Orscille Extract.—This may be adulterated with logwood or Brazil-wood extract. They may be detected, according to Leeshing, as follows: A solution of orseille extract, much diluted and acidified with acetic acid, will, if pure, when boiled with a freshly prepared solution of stannous chloride, become pale yellow or almost colorless, while logwood extract solution under similar circumstances will show a violet color and Brazil-wood solution a red color. If, therefore, the orseille is adulterated with logwood extract a permanent grayish-blue color will show, if with Brazil-wood extract, a reddish color.

Orseille is also found frequently to have been adulterated with aniline dyes, especially magenta, acid magenta, and methyl violet. For the detection of magenta and methyl violet Knecht\* employs cotton yarn dyed with chrysamin (p. 464). This does not take up the coloring matter of the orseille, but is dyed red by magenta and brownish-red by methyl violet. To detect the acid magenta, Kertesz† treats the orseille preparation with benzaldehyde and adds to the solution tin salt and hydrochloric acid, shaking up the mixture thoroughly. If acid magenta was present a red color will remain, while with pure orseille the solution remains colorless. One part of acid magenta in one thousand parts of orseille it is said can be thus detected. For other tests for the artificial dye-colors when present as adulterants in orseille,

<sup>\*</sup> Journ. für Prakt. Chem., 71, p. 19. † Berichte der Chem. Ges., xviii, p. 1970.

see Allen, "Commercial Organic Analysis," 2d ed., iii, pp. 322 and 323.

- (b) Quereitron Extracts.—The dyeing value of the extract, as well as a possible adulteration of the same with dextrine, glue, etc., can be best determined by an actual dye test. For this purpose, wool is boiled with 1.5 per cent. of tin salt and three per cent. of oxalic acid, then washed. One gramme of the wool is now dyed with twenty cubic centimetres of a solution of ten grammes of the quereitron extract in one thousand cubic centimetres of water. Similarly several portions of one gramme each of mordanted wool are dyed with solutions of pure bark or pure extract of definite strength, and the results compared.
- (c) Annatto (Orlean).—Annatto possesses only a slight importance as a dyeing agent, but special importance as the basis of most butter colorings. (See p. 299.) It is, therefore, a commercial article of common use and liable to be adulterated. The common adulterants are starch, dextrine, chalk, silica, alumina compounds and common salt, together with ochre, brick-dust. Most of these increase notably the percentage of ash, which in a pure sample it is said should not exceed ten to twelve per cent. Wynter Blyth gives the following two analyses as illustrating the nature of its adulteration:

Description.	Water.	Resin.	Extractive matter.	Asb.
Fair commercial sample Adulterated sample	24 2 13 4	28.8 11.0	24 5 27.3	22.5 48.8 Oxide of iron, alumina, silica, chalk, and salt.

For dyeing purposes the only satisfactory test is an actual dyeing test in comparison with an authentic unadulterated sample. For the analysis of the many butter-coloring mixtures containing annatto as the basis the reader is referred to Allen, "Commercial Organic Analysis," 2d ed., iii, pp. 353–356, and Wynter Blyth, "Foods, Composition and Analysis," p. 306.

(d) Logwood Extract.—Both the liquid and the solid extracts are liable to be adulterated, the former with glucose, molasses, dextrine, salt, and other extracts of lesser value, the latter with starch and inferior extracts. Notably are the French and German logwood extracts adulterated in the way just referred to. The following analyses of some of the commercial extracts as currently sold in France and Germany are given by V. H. Soxhlet:\*

DESCRIPTION OF EXTRACT.	Molasses.	Dextrine	Chestnut extract.	Salt.
Guaranteed Pure, 30° B Prima, 30° B	10 " " " " 20 " " " " " " " " " " " " " "	15 per cent. 10 " "	10 per cent. 15 " " 10 " " 15 " "	10 per cent.

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The Sanford Brand here referred to is a French extract made in imitation of the original American Sanford Extract.

The extracts may be tested for purity either by the colorimetric assay or by comparative dye tests. The colorimetric test is carried out, according to Henry Trimble,\* as follows: A volume of solution corresponding to .001 gramme of the *dry* extract is treated with ten cubic centimetres of water naturally or artificially containing traces of calcium carbonate and a solution of .002 gramme of crystallized copper sulphate. The mixture is brought quickly to the boiling-point and diluted with distilled water to one hundred cubic centimetres. The color of this solution is then compared with one of pure hæmatoxylin similarly used, or with a standard sample of logwood extract.

The method of carrying out the dye test for logwood with bichromate of potassium mordant has already been given in speaking of dyewoods. The same test is, of course, equally applicable to the extracts. Cotton strips are sometimes used for these dye tests instead of wool. The cotton strips must be boiled in dilute soda solution and well washed. They may then be mordanted with nitrate of iron solution instead of the chromium salt, following the nitrate of iron with a rinsing in carbonate of soda solution and thorough washing. They are then put in the dye-bath cold, and this gradually heated to boiling. In this dyetesting with iron solution, the hæmatoxylin of the solution is oxidized by the ferric oxide to hæmatëin, so that the full coloring value of the logwood is obtained in the test.

For the discovery of adulterations like chestnut extract, which contain almost nothing soluble in ether, Houzeau proceeds as follows: One gramme of the extract to be investigated is dried at 110° C., exhausted with ether, and the weight of the dissolved material determined. The undissolved material is then exhausted with absolute alcohol, and the weight of the portion dissolved by this also determined. The comparison of the figures so obtained with those yielded when a pure extract is treated with the same solvents will show clearly the presence or absence of adulterating extract. Dye tests may also be carried out with the material which has been extracted by ether and alcohol respectively in the two cases, and the difference more fully established.

(e) Catechu Extract.—Catechu is frequently adulterated, not only with mineral matter like sand and clay, but with starch, dextrine, sugar, blood, etc. The mineral matters will, of course, remain in the ash. This in normal catechu should not exceed five per cent. The starch may be detected by extracting the sample with alcohol, boiling the insoluble residue with water, and testing the cooled liquid with iodine, which will show by the blue color any starch present. An addition of alcohol to the aqueous solution will show by the production of a turbidity any notable quantity of dextrine. Blood may be detected by treating the sample with alcohol, and drying and heating the residue in a tube, when ammonia and offensive decomposition products will be given off, or the coagulation of the blood albumen when the aqueous solution is boiled.

<sup>\*</sup> Journ. Soc. Dyers, etc., i, p. 92.

The value of catechu for dyeing purposes can only be determined by a dye test. For this purpose strips of cotton-stuff are immersed for half an hour in a catechu solution (for each gramme of the cotton fifty cubic centimetres of a catechu solution containing five grammes to the litre of water are taken and diluted with water if necessary). The strips are pressed out, and then the color developed by oxidizing in a hot solution of one to two grammes of potassium bichromate to the litre of water.

- 3. For Cochineal.—The adulteration of cochineal may be effected in various ways. A very common adulteration is to admix with the fresh cochineal insects others from which the coloring power has already been in large part extracted. To give the exhausted cochineal insects the appearance of fresh ones, they are shaken up with tale, barytes, and white lead, and thus given a coating resembling the silvery insects. Either a washing or an ash determination will serve to detect this adul-The valuation of the cochineal as to coloring power may be made by several methods. The one best known is that of Penny,\* in which one gramme of the cochineal is treated with fifty grammes of dilute potassium hydroxide, twenty-five grammes of water added, and to this is then added drop by drop a solution of ferricyanide of potassium containing five grammes to the litre. The solution loses its purplishred color and becomes brownish-yellow. The action of the ferricyanide of potassium solution is tested in comparison on the solution of one gramme of a cochineal of known purity. Liebermann t extracts the cochincal with boiling water, and determines the coloring matter by the addition of a slightly acid solution of lead acetate. After filtering and washing the lead precipitate, a lead determination is made in an aliquot portion, and from this the percentage of coloring matter calculated. Allen does not consider either of these methods to be perfectly satisfactory. An actual dye test is therefore in the end to be regarded as the most reliable method of valuation. For this purpose strips of woollen stuff of about five grammes in weight are put into the bath until the color is all taken up. A portion of the strips may then be dyed scarletred by immersing them in a tin solution (for one gramme of cochineal two grammes of cream of tartar, two grammes of tin salt, and as much water as is needed to thoroughly immerse the strips), and the other portion of the strips may be dyed a cherry-red by the use of an alum solution (for one gramme of cochineal, three-fourths gramme of cream of tartar and one and a half grammes of alum). These strips are then to be compared with others obtained from similar treatment of a normal or pure cochineal sample.
- 4. For Indigo and its Preparations.—Indigo may be of very varying value as it comes into commerce, partly because of the differences natural to such a product and dependent upon the differences in cultivation of the plant, care in extracting and drying the indigo, and the fact that the natural product is at best a mixture, and partly from intentional adulteration. Thus starch colored with iodine, Prussian blue,

<sup>\*</sup> Journ. für Prakt. Chem., 71, p. 119. † Berichte der Chem. Ges., xviii, p. 1970.

smalt, and logwood-powder are said to be used as adulterants of commercial indigo. In order to detect the starch, the suspected sample is rubbed up in a mortar with chlorine-water until it is completely decolorized, when a drop of potassium iodide is added. If starch be present the blue color of iodide of starch will be seen. To detect the smalt or Prussian blue, the sample is oxidized with nitric acid, when if a blue residue is shown in the yellowish solution adulteration is indicated. If the adulterant were Prussian blue, the color fades too after a time, if smalt, it is permanent. To detect logwood-powder, mix the sample with oxalic acid, place it upon filter-paper, and moisten it; in the presence of logwood the paper will be colored red, if the sample were pure it is unchanged.

In the assay of commercial indigo the *moisture* is generally to be determined. This should not exceed some seven per cent. in a genuine sample. The *ash* similarly is an important criterion of the quality of the indigo sample. In the purest kinds it is sometimes as low as two per cent., but from five to eight per cent. is more usual. Some of the inferior grades of indigo, such as Kurpah and Madras, may contain from twenty-five to thirty-five per cent. of ash.

The methods for the determination of the percentage of indigo-blue are, of course, the most important things to be considered in connection with indigo as a dyeing material. They are very numerous. We may summarize the more important of them under three heads,—viz., oxidation methods, reduction methods, and sublimation of the pure indigo-blue from the commercial product.

The oxidation of the indigo-blue takes place in acid solution, the indigo being previously dissolved in strong sulphuric acid. Potassium permanganate, bichromate, and ferricyanide have all been recommended and used in this connection. All the processes are open to the objection that the oxidizing agents act on the indigo-gluten and ferrous salts as well as on the indigo-blue and indigo-red, but the errors due to this cause may be practically avoided, as pointed out by Rawson, by previously precipitating the sulphindigotic acid in the form of the sodium salt by adding common salt to the solution. The method with permanganate of potassium, modified in this manner by the use of common salt, is as follows: \* One gramme of the sample of indigo in the form of an impalpable powder is mixed in a small mortar with its own weight of ground glass. This mixture is gradually added with constant stirring to twenty cubic centimetres of concentrated sulphuric acid (specific gravity 1.845), which is then heated to about 85° C. for an hour. product is then cooled, diluted with water to one litre, and filtered from indigo-brown and other soluble matter. Fifty cubic centimetres of the filtered solution are now taken, diluted with fifty cubic centimetres of water, and thirty-two grammes of common salt added, which quantity is almost sufficient to saturate the liquid. After standing for two hours, the solution is filtered, and the precipitate washed with about fifty cubic centimetres of brine of 1.2 specific gravity. This sodium sulphindi-

<sup>\*</sup> Allen, Commercial Organic Analysis, 2d ed., iii, p. 308.

gotate is dissolved in hot water, the solution cooled, mixed with one cubi centimetre of sulphuric acid, and diluted to three hundred cubic centimetres. This solution is then titrated in a porcelain dish with a solution of potassium permanganate containing .5 gramme of the solid salt pelitre, the exact oxidizing power of which has been ascertained by experiment with a solution of pure indigotin. The oxidation is regarded a complete when the liquid which at first takes a greenish tinge change to a light yellow with a faint pink color on the margin.

The reduction of indigo-blue may take place in alkaline solution o with a solution of the sulphindigotic acid or its salts. Ferrous hydrox ide and hyposulphites are among the reducing agents used to effect th reduction in alkaline solutions. C. Rawson considers the hyposulphit reduction method the better one of the two. In carrying it out, on gramme of the finely-powdered sample is made into a paste with wate and placed in a flask with about six hundred cubic centimetres of lime water. The flask is closed by a cork having four perforations, two o which serve for the passage of coal-gas, a third carries a siphon, whil to the fourth is fitted a tap-funnel. The contents of the flask ar heated to 80° C. and one hundred to one hundred and fifty cubic centimetres of a strong solution of sodium hyposulphite (NaHSO<sub>2</sub>) intro duced through the tap-funnel. In a few minutes the liquid assumes yellow tint, and is maintained at a temperature near the boiling-poin for half an hour. After allowing the insoluble matters to subside, a aliquot portion of the solution should be removed, and a current of ai drawn through it for about twenty minutes, when it is acidulated wit hydrochloric acid. The precipitate, which consists of indigotin an indigo-red, is collected on a weighed filter, washed with hot water, drie at 100° C., and weighed. It is then exhausted with boiling alcoho whereby the indigo-red is dissolved out and the difference again weighe as indigo-blue. Rau reduces the indigo in alkaline solution with glu cose, and L. M. Norton uses milk of lime and zinc-dust as reducin agent, and then takes an aliquot portion of the reduced solution to re duce a solution of iron-alum. The ferrous salt formed corresponds t the reduced indigo in the volume taken, and is determined by titratio with a standard solution of potassium bichromate. (For details, se Helen Cooley's article, Amer. Journ. Anal. Chem., ii, p. 133.)

For the reduction of the indigo in acid solution, Bernthsen an Drew\* recommend the use of hyposulphite of soda (NaHSO<sub>2</sub>), an claim that the reaction is a quantitative one:  $C_{10}H_8N_2O_2(SO_3H)_2$  - NaHSO<sub>2</sub> +  $H_2O = C_{16}H_{10}N_2O_2(SO_3H)_2$  + NaHSO<sub>3</sub>.

C. Rawson † considers that of all the volumetric methods which have been devised for estimating indigotin the hyposulphite process is capab of giving the most rapid and accurate results, but that considerab care and delicacy are required in its manipulation.

Lee ‡ has proposed the sublimation of the indigo-blue as a method for determining its percentage in commercial indigo. Other writer

<sup>\*</sup> Chem. News, xliii, p. 80. + Allen's Com. Org. Anal., 2d ed., iii, p. 309.

<sup>‡</sup> Chem. News, l, p. 49.

REACTIONS OF THE MOST IMPORTANT NATURAL DYESTUFFS.

DYESTUFFS.	Aqueous extract.	Caustic sods, 1:10.	Aluminum sul- phate and sodium carbonate, 1:10.	Ferric chloride, 1:10.	Calcium chloride, 1:10.	Hydrochloric acid, 1:10.	Remarks.
MADDER	Dirty red.	Bluish red.	Red.	Dark brown pre-	Red precipitate.	Red precipitate.	
SANDAL-WOOD	No extraction.	Bluish-red extract.	Red.	Brown-black pre-	Red precipitate.	Red precipitate.	With alcohol,
Говтоор	Bluish red.	Violet precipitate.	Reddish-violet so- lution.	Elack solution.	Red precipitate in concentrated so-	Yellowish-red color.	reddish extract.
OLD FUSTIG	Reddish yellow.	Violet precipitate.	Yellow solution.	Black precipitate.	Red precipitate in concentrated so-	Yellow-red color.	:
Young Fusino	Red solution,	Bluish-red color.	Reddish-yellow so-	Dark olive precipi-	Red precipitate.	Bright yellow	:
QUERCITRON	Reddish yellow.	Red color.	Yellow precipitate.	Dark green precipi-	Yellow precipitate.	Bright yellow	Flavine.
TURMERIO	Yellow solution.	Red color.	Yellow precipitate.	Yellow precipitate.	Yellow precipitate.	Bright yellow	:
ANNAFTO	Yellow solution.	Yellow color.	Yellow solution when poured	Black precipitate, turning blue with	Red precipitate.	Red color.	Dyes cotton in alkaline solu-
САТЕОНО	Turbid yellowish- brown solution.	Clear reddish-yel- low color.	over. Yellow color.	sulpnuric acid. Dark green precipi- tate.	Yellow precipitate.	Bright yellow precipitate.	With potassium luchromate, red-brown on
PREPARED CATECHU.	Clear yellowish- brown solution.	Reddish-brown precipitate.	Yellow color.	Bright olive color.	Yellow precipitate.	Bright yellow precipitate.	heating. With potassium bichromate,
GALLNUTS	Dirty yellow color.	Reddish-yellow precipitate.	Light yellow color.	Blue-black precipi-	Turbidity.	Bright yellow	yenow-prown.
SUMACH	Dirty yellow color.	Reddish-yellow	Yellow color.	Black precipitate.	Yellow precipitate.	Bright yellow	:
COURINEAL	Bluish-red color.	Bluish-red solution.	Red color.	Black color.	Black precipitate.	Yellow-red color.	:
TANNIN	Colorless.	Light yellow pre-	Light yellow pre-	Blue-black precipi-	Turbidity.	Bright yellow	
LAC DYE	Red color.	Bluish-red solution,	Red color.	dray precipitate.	Red precipitate in concentrated so-	recipitate. Yellow color.	
CUDBEAR	Bluish-red color,	Bluish-red solution.	Bright red color with aluminum sulphate.	Bright red color.	lution. Red precipitate in concentrated solution.	Yellow-red color.	Orseille,

however, do not agree that, unless the indigo has previously been som what purified, the results can be depended upon.

C. Rawson \* has given the following results with commercial sar ples, using the several processes just detailed:

METHOD USED.	Java.	Bengal.	Bengal.	Oude.	Kurpah.	Madras
Water	2.99 1.99 60.84	5.22 8.91 57.50	6.17 4.86 49.36	7.50 8.21 41.60	8.05 25.72 41.92	5.71 38.62 39.56
Indigotin, volumetric, by hypo- sulphite	68.78	59.26	55.66	43.18	42.52	86.80
sulphate and NaOH Indigotin, gravimetric, by hypo-	68.24	58.84	54.84	44.50	41.50	34.50
sulphite and lime	$\left\{ egin{array}{c} 68.97 \\ 4.23 \end{array} \right\}$	${3.50 \atop 3.50}$	$\{ \begin{array}{c} 56.20 \\ 2.80 \end{array} \}$	$\left\{ egin{array}{c} 48.42 \\ 8.65 \end{array} \right\}$	42.68 2.45	$\left\{ egin{array}{c} 85.21 \\ 8.98 \end{array} \right\}$
with KMnO, direct	76.18	66.71	62.66	50.04	47.15	89.50
after precipitation with salt	78.55	63.50	57.50	44.90	43.10	87.40

The table from Dammer's Chem. Technologie, Band iv, p. 591 (se opposite page), shows the characteristic reactions of the important na ural dyestuffs.

## V. Bibliography and Statistics.

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<sup>\*</sup> Allen, Commercial Organic Analysis, 2d ed., iii, p. 311.

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#### STATISTICS.

1. Indigo, Natural and Artificial.—The exportations of natural indigo from British India have decreased greatly owing to the introduction of synthetic indigo. The exports from British India were:

1896	169,500	cwt.	Value	43,700,000	rupees.
1901-02	89,750	"	"	18,522,554	66
1903-04	60,410	**	66	10,762,026	EL
1904-05	49,256	**	"	8,346,073	66
1905-06	31,186	**	"	5,863,777	66
1906-07	35,102	66	"	7,004,773	**

The area under cultivation for the indigo plant in British India (Bengal, Madras, Agra, Oude, Punjab) was in:

1896	 1,600,000	acres
1906	 450,000	acres

The production of synthetic indigo has grown during the same period as follows:

1900	1873	tons	1904	8730	tons
1901	2673	tons	1905	11165	tons
1902	5284	tons	1906	12733	tons
1903	7233	tons			

2. EXPORTATIONS OF DYE-WOODS.—The exportations of several of the more important dye-woods from tropical American countries for the period given have been as follows:

## 1. Logwood Exports:

	Fron	Haiti.	From	Jamaica.
	Pounds.	Value.	Pounds.	Value.
1882-83	 152,288,713	\$1,998,789	66,685,584	\$434,632
1883-84	 154,775,887	2,031,434	100,638,496	655,921
1884-85	 142,986,254	1,876,695	126,795,200	743,774
1885-86	 114,341,436	1,500,731	142,256,128	927,165
1886-87	 105,000,065	1,378,125	132,009,472	932,089
1887–88	 106,163,734	1,393,399	226,108,912	1,718,627
1888–89	 57,021,431	748,406	258,616,960	1,826,035
1889-90	 70,801,241	929,266	133,232,400	962,432
1890-91	 56,743,891	744,764	244,794,592	1,861,395
1891-92	 39,766,320	521,933	194,152,784	1,476,320
1892-93	 		207,472,832	1,633,947

## 2. Fustic Exports:

	•	From Mexico.		From Jamaica.	
	• •	Pounds.	Value.	Pounds.	Value.
1882-83		30,746,240	\$280,988	7,477,792	\$48,738
1883-84		32,995,200	248,656	4,024,272	21,857
1884-85		17,471,509	128,019	2,078,160	13,093
1885-86		17,420,099	110,873	3,526,768	21,071
1886-87		24,942,407	178,621	9,366,000	61,044
1887-88		26,583,858	177,488	5,518,016	35,964
1888-89		18,224,030	133,952	2,777,216	10,425
1889-90		23,762,671	198,646	1,457,200	8,606
1890-91		16,927,020	119,631	2,128,112	12,714
1891-92	•	13,187,368	96,588	1,517,152	9,888
1892-93				14,472,976	102,190

## 3. Exports of Brazil-wood from Bahia during recent years were:

	U	To nited States. Kilos.	To England. Kilos.	To Germany. Kilos.	To France. Kilos.	All other countries. Kilos.	Total Kilos.
1884		584,318	143,480	15,000	336,189	56,350	1,135,337
1885		232,912	292,212	49,568	703,497		1,278,189
1886		684,002	193,189	134,857	904,348	18,569	1,934,965
1887		783,616	152,453	46,640	1,374,543		2,357,252
1888		388,631	84,341	18,584	369,725		861,280
1889		149,063	82,156	753,457			984,676
1890		58,121	166,198	78,959	127,016		430,295
1891		251,873			670,857	21,321	944,051
1892		635,030	64,676	25,782	1,093,650		1,819,138
1893		615,158	517,937	147,177	548,734	8,970	1,837,976

# 3. Importations of Dye-woods and Dye-wood Extracts into te United States.

	1906.	1907.	1908.	1909.	1910.
Annatto extract (lbs.)	281,575	651,595	551,872	711,191	619,37
Valued at	\$22,156	\$51,128	\$40,708	\$48,839	\$39,57
Cochineal (lbs.)	111,007	184,326	152,624	102,694	150,81
Valued at	\$53,446	\$84,911	\$54,146	\$33,875	\$41,4
Fustic (tons)	5,783	3,483	4,452	2,466	5,8
Valued at	\$89,513	\$54,765	\$53,884	\$34,752	\$82,88
Gambier (lbs.)3	1,478,837	28,853,124	26,692,100	31,000,855	25,808,7:
Valued at	31,118,910	\$977,000	\$895,210	\$1,313,990	\$1,264,05
Indigo, crude (lbs.)	7,196,678	7,170,836	6,078,073	6,249,975	7,636,69
Valued at		\$1,233,515	\$1,058,354	\$1,400,000	\$1,195,94
Indigo, extract (lbs.)	125,257	145,339	140,291	148,454	142,8;
Valued at	\$7,698	\$8,013	\$14,391	\$17,897	\$16,4;
Logwood (tons)	36,624	37,901	21,809	17,873	31,2
Valued at	\$498,602	\$478,656	\$248,578	\$166,371	\$353,3
Logwood and other dye-			•		, ,
wood extracts (lbs.)	3,443,676	4,542,257	3,576,676	3,463,582	2,937,69
Valued at	\$295,188	\$368,704	\$230,475	\$231,612	\$187,1:
Madder, ground (lbs.)	45,991	62,633	50,856	37,910	30,70
Valued at	\$4,600	\$5,721	\$5,249	\$3,019	\$2,3
Orchil, value	\$33,980	\$31,880	\$29,924	\$45,818	\$38,70
Saffron, extract of, value	\$59,964	\$74,468	\$70,509	\$67,648	\$80,70
		(Commerce	and Navigat	ion of U.S	

#### CHAPTER XIV.

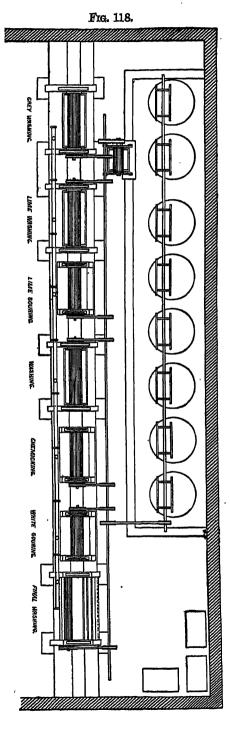
### BLEACHING, DYEING, AND TEXTILE PRINTING.

PRELIMINARY.—Prior to the operation of bleaching, especially in cases where delicate shades are required, it is always necessary to thoroughly cleanse the fibre or fabric of grease and dirt. For cotton, which is generally handled as hanks, warps, and pieces, it is sufficient to boil it in a dilute solution of caustic soda or soda ash, followed by a good rinsing: it may, in some instances, be boiled in plain water, wrung out, and bleached or dyed; ordinarily, however, a boiling for two or three hours in a bath of eight to ten per cent. of crystallized soda and one to two per cent. of soap, calculated to the weight of the cotton, yields good result. The time for boiling out cotton is much reduced if it is immersed in a weak lukewarm bath of two per cent. sulphated oil strongly neutralized with ammonia or in a soap-bath containing ammonia. This is found to completely remove all natural oil on the fibres and thoroughly wet them. Wool is always thoroughly scoured both before and after it is manufactured into yarn. The soap solution generally employed contains from four to five ounces to the gallon of water, accompanied usually with a carbonated alkali (potash or ammonia) in about the following proportion: ten per cent. of soda and two per cent. of soap. The temperature of the bath is about 40° to 50° C. (See p. 343.) For silk (see p. 349) the boiling off contains about twenty-five to thirty pounds of Castile. Marseilles, or other neutral soap for each hundred pounds of silk, and a temperature at or near the boiling-point is taken for about two hours, turning the silk occasionally. For some colors a second boiling off can be employed to advantage, only one-half the quantity of soap being used as in the first bath. It is the practice to use the baths several times, care being taken to enrich them with fresh soap.

A. Bleaching.—This highly-important operation results in a more or less complete destruction of the natural coloring matter which is found in all fibres of industrial importance. Owing to the somewhat powerful action of most of the agents employed for the purpose, it will appear that, unless care and discretion are applied to their use on the part of the bleacher, something more than a destruction of the coloring matter will occur,—a probable partial destruction of the fibre. The operation has been known since the earliest times; the white linens of the Egyptians and Phænicians were much esteemed by the nations trading with them. In the early part of the eighteenth century immense fields were given up wholly to bleaching in the United Kingdom; the process as carried out required several months, consisting of a successive treatment of the cloth or fabric in alkaline solution—termed "bucking"—and washing, then exposing, while damp, and spread out on the grass to the

sunlight for a few weeks (crofting), immersing in sour milk, washing again, and finally exposing on the grass, these several operations being repeated until the required degree of whiteness is obtained. Great improvements in the above tedious process resulted when the use of sulphuric acid was substituted for the sour milk, and chlorine gas replaced the lengthy field exposure, this latter being due to M. Berthollet: but the general use of this substance was not established until the manufacture of the now familiar "chloride of lime" or "bleach." Since then many other bleaching agents, notably, hydrogen peroxide, have peared, but whether they will ever displace the above is an uncertainty.

1. Cotton in the raw or unmanufactured state is seldom bleached except in the production of absorbent cotton; as yarn, however, it is continually. hanks, which have been previously scoured, are worked in a solution of chloride of (chemick) from one to two hours. washed well in water, and passed through dilute sulphuric acid (1° Tw.) for about half an hour, and finally well washed. These operations can be easily conducted in the ordinary wooden tubs of the dye-house in places where much yarn does not have to be bleached, otherwise special arrangements should be provided. Cotton warps are similarly treated, the apparatus employed being a continuous (warp) dyeing-machine. Cotton fabrics require much care and skill, especially those intended for domestic



use in the bleached condition, and also those which are to be afterwards dyed or printed with delicate shades. The method of bleaching, which has reached a high state of perfection, is the so-called "madder-bleach," from the fact that it is employed on all piece goods to be printed with alizarin. The process detailed and illustrated below must not be accepted as the exact method followed in every establishment,—it being remembered that nearly every bleacher has his own modifications which he introduces, but all yield the same result. The operation of stamping or sewing on designating marks; sewing the pieces together and singeing,—a removal of the nap or down from the cloth by means of a gas flame or curved hot plate ("singeing plate"),—need not be detailed here; reference may be had to special works on textile manufacture.

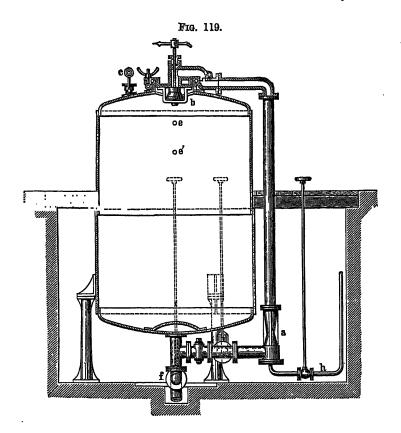
Fig. 118 is a plan of part of a bleach-house for cotton cloth. The goods being received, they are passed through the first washing-machine, on the left of the figure; this operation has for its object the removal of loose dirt, grease,—added to the fabric during weaving,—and other matters; usually the goods are stacked overnight in order to allow an incipient fermentation to take place, when they are passed several times through the *lime-wash* (milk of lime) in order to become thoroughly impregnated with about five per cent. of lime, this being accomplished by means of rollers immersed in and below the surface of the lime-bath and a pair of squeezing or "nipping rollers."

Following the liming operation is the boiling ("bowking") in kiers; these are strong, wrought-iron cylindrical vessels, provided with a series of pipes, and in some cases with injectors, which enable the liquids contained in them to circulate completely through the cloth, which is previously introduced in the form of a rope. Fig. 119 is a vertical section of a single injector-kier, and one well adapted for working at low pressures. Reference being had to the figure, the vessel being filled with the fabric, which is well laid in, the liquid is admitted, gradually finding its way to the false bottom, through which it passes to the injector at a, where it meets a steam current, which forces it upward through the large pipe, finally being admitted to the kier again through the valve b, repeatedly following the circuit.

Barlow's high-pressure kiers are usually worked in pairs, and the liquid is forced from one to the other by the aid of steam. This kier has a central perforated tube, through which the liquid passes to come in contact with the cloth. Several other forms of kiers are in use, even open kettles acting as such, the object being the same in each case.

The length of time the cloth remains in the kier varies considerably: in some establishments, where a high-pressure is used (forty to fifty pounds per square inch), less time is required,—five to six hours being deemed sufficient; again, where a low-pressure is used (eight to twelve pounds) the goods are allowed to remain in from ten to twelve hours. From this boiling the pieces are washed in water, and passed through dilute hydrochloric acid (specific gravity 1.01 = 2° Tw.),—the bath being technically termed a "sour." The pieces are slowly worked until

the lime is completely dissolved, when the goods are thoroughly washed, or until every trace of acid is removed, when a boiling with soap and soda follows in kiers exactly as in the boiling previously mentioned. For each hundred pounds of cloth a resin soap is used, made with five to six pounds of soda ash and one to two pounds of resin; the soda is dissolved in two gallons of water, the resin added, and the whole boiled for several hours; for each pound of cloth to be acted upon one gallon of water is used. The time required for this boil is nearly the same



as in the previous boiling. When the resin soap solution is run off, the goods are boiled for three or four hours with a one per cent. solution of soda, to remove the soap and any unconverted resin remaining, followed immediately by a wash. At this stage of the process occurs the real whitening, or bleaching, of the goods,—the so-called "chemicking,"—requiring much care, and is performed with a solution made by dissolving chloride of lime, allowing to settle and become clear, the supernatant liquor alone being used. The strength of the solution, varying from ¼° Tw. to 2° Tw. (specific gravity 1.001 to 1.01), being used cold, or but slightly warmed, in the latter case penetrating the

cloth better. Repeated passage of the goods through a weak solution is preferable to a shorter time in a strong solution, the danger from injury to the pieces being less. The next operation may be (not always) a wash, and then a souring in dilute (specific gravity 1.01) sulphuric acid,—termed a white sour,—after which the goods are allowed to remain for some time in a heap, but not long enough to become dry, as a tendering of the cloth will result; this is followed with a final wash to remove every trace of acid, passed through squeezing rollers, and over revolving cans heated by steam, to dry. The length of time required in the above process varies; if the goods are to receive a fine clear bleach, or are to receive delicate shades in dyeing and printing, four or five days may be necessary, but in the event of the goods being intended for full shades, half the time will answer.

Mather-Thompson's Process.—This is one of the newer processes, and is admirably suited for warps and piece-goods. The goods are sewed together, or tied, in the case of warps, subjected to the action of hot caustic alkali, washed, and transferred to wagons, the sides of which are of iron lattice-work (cages), and pushed into a horizontal kier, and for five hours acted upon by a solution of caustic soda (2° to 4° Tw. = specific gravity 1.01 to 1.02) delivered in a spray and at a pressure of four to five pounds. Without removing the goods from the kier they are washed with hot water, removed, and rinsed with cold water, completing the scouring. The bleaching is carried out in a continuous apparatus through the following stages:

- 1. Rinsing with warm water.
- 2. First chemick bath (chloride of lime solution, 1° Tw. = specific gravity 1.005).
  - 3. Passage through atmosphere of carbonic acid gas.
  - 4. Washing with cold water.
  - 5. Worked through a one per cent. soda solution at 175° F.
  - 6. Second washing.
  - 7. Second chemick (chloride of lime solution .5° Tw.).
  - 8. Second passage through carbonic acid gas.
  - 9. Third wash.
- 10. Through one per cent. hydrochloric acid, or through one per cent. of a mixture of hydrochloric and sulphuric acid (2:1).
  - 11. Final wash.

In this process the real bleaching is effected by the hypochlorous acid liberated by the action of the carbonic acid gas upon the calcium hypochlorite.

Lunge's Bleaching Process differs but slightly from others using chloride of lime, except that he increases the bleaching action by the use of a small quantity of some organic acid,—preferably acetic. Chloride of lime in contact with acetic acid forms calcium acetate, with evolution of free hypochlorous acid; this gives up oxygen during the bleaching, leaving hydrochloric acid, which acts on the calcium acetate, forming calcium chloride and regenerating the acetic acid. The hydrochloric acid never being in the free state cannot act on the fibre; acetic

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acid has no action, even at the high temperature or pressure used in bleaching.

Hermite Process for Electrolytic Bleaching.—This process is probably one of the most successful yet brought forward, embodying the use of electricity, effecting the bleaching by the decomposition of a four to five per cent. solution of chloride of calcium (not "chloride of lime," or "bleaching-powder"), of magnesium, or of aluminum. The electrolyzed solution of the salt employed is of especial service in causing the destruction of the coloring matter of vegetable fibres, but, owing to the peculiar effect of chlorine on wool or silk, it is impracticable with them. Electrolyzed salt solutions are replenished by the addition of a quantity of salt equal to that absorbed by the fibres or fabrics when withdrawn from the bleach-bath.

- 2. Linen.—This fibre is much more subject to the destructive action of bleaching agents than cotton, in consequence of which the same process is not applicable, and also on account of the greater amount of impurities present, chiefly pectic acid. For yarns the trade distinguishes three important grades of bleaching,—half, three-quarters, and full white, to obtain which several operations are necessary:
- 1. Boiling for three or four hours in a ten per cent. solution of soda ash, or in a six per cent. solution of caustic soda. Wash, rinse, and pass through squeezing rollers.
- 2. Pass through a .4° Bé. solution of chloride of lime, and work or recl one hour, and wash.
- 3. Transfer to dilute sulphuric acid for one hour (one part acid to two hundred parts water).
  - 4. Boil again in a kier with two per cent. caustic soda.
  - 5. Repeat the passage through chloride of lime and wash.
  - 6. Final treatment with sulphuric acid as in No. 3.

The above will produce a half-bleach, and by repeating the three final operations a full white will be obtained. Recling is a term particularly applicable to linen-bleaching, owing to the way the yarn is handled, the result being that the carbonic acid in the air acts upon and decomposes the chloride of lime, setting free hypochlorous acid, similarly to the use of the gas in the Mather-Thompson process.

Linen cloth, despite many trials, still requires much longer time to successfully bleach than yarn. It is quite possible to bleach the cloth in a comparatively short time, but the strength of the fibre would be weakened. The following outline of the general process indicates the successive stages:

- 1. Liming. Boil with eight to ten per cent. for fourteen hours and wash.
- 2. Allow to remain in dilute hydrochloric acid (specific gravity 1.012) for four to six hours and wash.
- 3. Boil with resin soap (two pounds caustic soda and two pounds resin) for ten hours, followed immediately by a boiling for six to eight hours with one pound caustic soda.
  - 4. "Grass." Expose on the fields for a week or more.

- 5. "Chemick." Pass through chloride of lime solution of ½° Tw. for about five hours and wash.
- 6. "Sour." Steep in dilute sulphuric acid 1° Tw. for two to three hours and wash.
- 7. Boil for four to five hours with .5 to .75 per cent. of caustic soda, wash, and
  - 8. Expose again for four to five days in the fields.
  - 9. Second chemick. Same as No. 5, only 1/4° Tw. for five hours.
- 10. If necessary, rub with a soft soap between "rubbing-boards" to remove brown spots.
  - 11. Expose again on the grass as before.

The frequent exposure of the goods on the grass to the combined action of moisture, air, and light necessarily dispenses with a certain amount of the chloride of lime, besides allowing of a less energetic action.

- 3. Jute.—A good white on this fibre is difficult to obtain. Prior to bleaching, jute is scoured with a five per cent. solution of sodium silicate (soluble glass) at 70° C., washed, and bleached with a solution of sodium hypochlorite containing about one per cent. of available chlorine, made by decomposing bleaching-powder with carbonate of soda, settling, and using the clear liquid. The goods are thoroughly washed, and treated in a dilute bath of hydrochloric acid (½° to 1° Tw.) and washed, or they can be further acted on by sulphurous acid by immersing in a bath of sodium bisulphite for two to three hours and dried. Jute can also be bleached by being worked in a solution containing one per cent. permanganate potash (calculated to the weight of its material) and exposing to the air until it becomes brown, when it is immersed in a solution of sulphurous acid and washed.
- 4. Wool.—For yarns, the oldest practical method of bleaching is "stoving,"—that is, an exposure of the damp goods to the vapors of burning sulphur, confined, usually, in a frame building; in the centre of the floor is mounted an iron pot in which roll sulphur is placed, and ignited by a piece of iron heated to redness. From six to eight per cent. of sulphur is consumed, and the time required is about eight hours, but for carpet yarns and goods of a similar grade twelve hours may be necessary. The yarn is removed and well washed, the water containing, possibly, a little carbonate of soda to neutralize any sulphurous acid remaining.

For piece-goods the same process is applicable, but it requires arrangements for passing the fabric over rollers inside the sulphur-house at a uniform rate. Piece-goods can also be bleached according to two somewhat lengthy processes, embodying the sulphuring in chambers, detailed in Sansone's "Dyeing," vol. i, p. 123.

The wool bleaching process based upon the action of the peroxides of sodium or hydrogen is the most important. No metal should be exposed in the wooden vats in which the bleaching is performed, and care

<sup>\*&</sup>quot;Rubbing boards" are two fluted pieces horizontally placed, the upper of which is moved in opposite direction to the course of the cloth.

should be taken to see that no sediment is in the water-supply pipe, all such taking up oxygen from the reagent and thus weakening it. A solution of hydrogen peroxide (equal to about one per cent., and capable of destroying six cubic centimetres of decinormal potassium permanganate solution) is made up in the vat, and this is carefully neutralized with silicate of soda which has been previously diluted with warm water; the yarn or goods is immersed and kept below the surface of the liquid by means of a wooden lattice frame. The temperature must not be above the normal. In a few hours the wool will be bleached to a white or nearly so, and by keeping it immersed a "wool white" will be obtained, after which the material is lifted, and allowed to drain back into the vat, when the liquid is brought up to the original strength with fresh peroxide. The bath can be kept in use for six months. After draining, wash in water containing a trace of sulphuric acid, finally with water alone.

5. Silk.—The preliminary operations for treating this substance have already been mentioned. Ordinarily, silk is treated in a similar manner to wool, being hung on poles in an atmosphere of sulphurous acid for several hours (four to six), taken down and washed; or the silk can be worked in a bath of bisulphite of soda, followed by a weak alkaline wash and a final rinse. Aqua regia (hydrochloric acid and nitric acid, 5:1) of 3° to 4° Tw., and at 70° Fahr., is much used for small lots; the silk being constantly worked for about twenty minutes when the bleaching is finished. For very fine tints, the silk is entered into a soap-bath heated from 85° to 105° Fahr., wrung out, and bleached according to the peroxide process as indicated above for wool, but employing solutions of greater strength.

Tussah silk is always bleached with hydrogen peroxide, being immersed, as in the case of wool, for several hours, or even days. When the necessary degree of whiteness is obtained, the silk is rinsed and dried. Sansone mentions immersing the silk in strong peroxide, wringing out the excess, and steaming in a closed vessel. This method has yielded good results.

B. Bleaching Agents and Assistants. — Chloride of Lime ("Bleaching Powder"), the most important agent for bleaching purposes, is produced in immense quantities by acting on dry slaked lime with chlorine. It occurs in commerce as a white powder possessing a characteristic odor resembling that of chlorine, and if exposed rapidly absorbs moisture. The real strength depends upon the amount of available chlorine obtainable,—ranging between twenty-two and thirty-five per cent. Solutions of the above sold under fanciful names are met with in the trade varying in strength from five to eight per cent. "Chlor-ozone" is a product considerably used, and is essentially a solution of sodium hypochlorite.

Permanganate of Potash (K<sub>2</sub>Mn<sub>2</sub>O<sub>3</sub>), although not strictly a bleaching agent, is mentioned on account of its very high oxidizing properties.

Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>) is a colorless, odorless liquid obtained

by the action of hydrofluoric acid upon barium peroxide in a lead-lined

tank. The operation is conducted at as low a temperature as possible, and with continuous stirring; in about twelve hours the reaction is over, and the supernatant liquid drawn off and preserved. The residue, barium fluoride, is decomposed with sulphuric acid, and the hydrofluoric acid recovered. It is customary to refer to the strength of hydrogen peroxide as being of so many volume capacity, six, ten, etc.; this means that one volume of the peroxide will yield six, ten, etc., volumes of oxygen gas.

Sodium Peroxide, or Sodium Dioxide (Na<sub>2</sub>O<sub>2</sub>), is now an important substitute for hydrogen dioxide, as it is in many respects more convenient to use and can be kept, when properly sealed from the air, for a long time. It is a yellowish-white powder, and can be used in alkaline or acid solution.

Soda Ash (Na<sub>2</sub>CO<sub>3</sub>).—This is the commercial anhydrous carbonate of soda, used principally in scouring. It is generally contaminated with varying percentages of caustic soda, sodium chloride, sulphate, etc. Its value depends on the amount of Na<sub>2</sub>O contained.

Sal Soda (Na<sub>2</sub>CO<sub>3</sub>.10H<sub>2</sub>O) and Concentrated Sal Soda (Monohydrated, Na<sub>2</sub>CO<sub>3</sub>.H<sub>2</sub>O) are much purer and more expensive carbonates; they contain no caustic soda, which renders them well suited to scouring.

Caustic Soda (NaOH).—It comes in trade in iron drums—solidly filled—or in a coarse powder. It is obtained by treating carbonate of soda with milk of lime, whereby the carbonate is decomposed with formation of calcium carbonate, when the clear liquid is drawn off and evaporated down to the solidifying point.

Carbonate of Potash (K<sub>2</sub>CO<sub>3</sub>) is not used in the dye and bleach works to the same extent as soda, although for silk- and wool-scouring it leaves the yarns, etc., with a better "feel," and when used in soaps, it does not cause colors to run or "bleed" to the same extent as soda. Its value depends upon the percentage of carbonate.

Acids.—The mineral acids are used in bleaching chiefly to neutralize alkalies, or to cause a disengagement of hypochlorous acid in the so-called "sours," and reference to their production is unnecessary. Hydrochloric Acid of commerce (also called Spirit of Salt, or Muriatic Acid) is yellow in color, due to impurities. The general strength is 21° B6. (specific gravity 1.17). Nitric Acid, used in conjunction with the above for silk-bleaching, and largely in the preparation of some mordants, is bought with a gravity of 17.7° B6. (specific gravity 1.140). Sulphuric Acid (H<sub>2</sub>SO<sub>4</sub>) is obtained by the burning of sulphur and conducting the gas into lead chambers, in contact with nitrous vapors and steam. It is a heavy, oily-looking liquid, and when pure is colorless. It is ordinarily sold at 66° B6. (specific gravity 1.84).

Soaps.—The soaps employed in bleaching, etc., embrace Tallow, Resin, and Olive Oil (for silks), although others are used, but mainly for special purposes. Reference to them has been made in the chapter on Oils and Fats. (See p. 68.) In most large establishments soapboiling appliances are in use.

C MORDANTS EMPLOYED IN DYEING AND PRINTING.—The process of

mordanting is of the utmost importance, having for its object the precipitation of some substance upon the fibre which has an affinity for, and will effect a more or less complete fixation of, the coloring matter used for the dyeing. The nature of the mordanting substance used depends upon the character of the fibre, the kind of dye, and upon the effect sought; some shades require the use of several. Under ordinary circumstances wool is simply boiled in a solution of a metallic salt, for example, bichromate of potash ("chrome"), in the presence of a small quantity of some acid, in this case, preferably, sulphuric. Wool so treated is said to be chromed, and is in a condition to be dyed with logwood or with colors of the anthracene group. Silk is mordanted similarly, lower temperatures, however, being employed. If silk and wool are immersed for a time in a solution of a metallic salt, an absorption will take place, when the fibre can be washed in water, during which operation a deposition of a basic oxide will occur. Cotton, unlike wool or silk, has but little natural affinity for the majority of coloring matters, and of necessity must be specially prepared. It is well known that cotton has a strong tendency to combine with tannic acid, and this is made use of by steeping cotton in a solution of sumach extract, catechu, or other tannin-yielding material; if it is afterwards washed and worked in a bath of some soluble metallic salt, an insoluble compound will be formed, which then has the property of uniting with the dve. It is not always necessary to prepare the cotton with tannin, an immersion in the mordant, followed by an oxidation or ageing, being deemed sufficient.

Substantive Dyeing is where the coloring matter is taken up from its solution by the fibre without the assistance of any agent. Wool and silk are dyed with the coal-tar dyes in this manner, using some sulphate of soda and sulphuric acid in the case of the former, and with a soapbath and a little acetic acid in the case of the latter. Cotton, when dyed with the benzidine colors, also comes under this head; it is possible a colored compound of cellulose and the base of the dye is formed. The use of salts in dyeing the above is merely to prevent a too rapid absorption of the dye by the fibre, thereby obviating uneven shades.

Adjective Dyeing necessitates the intervention of mordants, as above explained. Albumen, however, does not cause the formation of an insoluble precipitate on the fibre, but causes the cotton fibre to behave towards the dye in a manner similar to wool. Many coloring matters already fixed on cotton have the valuable property of serving as mordants for other dyes, a property much employed in the production of compound shades.

The following lists of mordants embrace only those of prominence and in general use; exact methods for their manufacture will be found in the works of Hummel, Sansone, Herzfeld, and others.

(a) Mordants of Mineral Origin.—Tin Mordants.—These are first in importance to the dyer and printer. They are used in two states of oxidation, stannous and stannic. The former salts have a great affinity for oxygen, a property of considerable value as a discharge for other colors. Their solutions are colorless or nearly so except these prepared

with nitric acid, which are yellowish,—due, possibly, to an incomplete oxidation of the tin. The most prominent tin compound is Stannous Chloride,—when crystallized, "tin crystals," or as a liquid known as "single muriate of tin," or "double muriate of tin," according to the gravity. The crystals are obtained by dissolving feathered tin in commercial hydrochloric acid and evaporating; good samples contain about fifty per cent. of metal. The impurities are iron, lead, and sometimes copper. Stannic Chloride (SnCl<sub>4</sub>) is of great importance not as a mordant but to the silk dyer as a weighting agent. It is produced in immense quantities, and sold under the name of "dynamite."

Tin Spirits, owing to the advent of the tar-colors, are much less used than formerly. Their composition was exceedingly variable, consisting usually of stannous chloride, with or without additions of sulphuric, oxalic, tartaric, and nitric acids, and they bore such names as Amaranth Spirit, Yellow Spirit, Finishing Spirit, etc. "Stannous Nitrate" (nitrate of tin) is essentially a solution of tin in nitric acid, the chemical composition of which is doubtful. "Tin spirits" is a collective name for a long list of stannic compounds, made, usually by the dyer, by the aid of hydrochloric and nitric acids, sodium and ammonium chlorides, etc. They are no longer used. Stannate of Soda, or Preparing Salt, is used in cotton- and woollen-printing; its value depends upon the amount of stannic oxide contained.

Alumina Mordants.—Sulphate of Aluminum, also known as Patent Alum, does not find much application in the dye-house, except in connection with the tin weighting process for silk, on account of its value in causing a plumping of the fibre. It is obtained from the mineral bauxite, and from cryolite. The brand manufactured for paper-makers is the purest, containing but little or no iron. By the addition of alkaline carbonates the normal aluminum sulphate is changed into a basic sulphate which yields alumina to the fibre more readily. Their application to cotton is followed by a treatment with ammonia or soap to fasten the alumina more fully, to wool generally with cream of tartar, and to silk by immersion overnight in the solution, followed by a washing, which causes the formation of a basic salt. Aluminum Acetate, or "Red Liquor,"—so called from the original use to which it was put, dyeing reds,-is obtained by the double decomposition of aluminum sulphate and calcium or lead acetate in the proper proportions, and using the supernatant liquid. Professors Liechti and Suida, and Köchlin have conducted elaborate researches into the action of the aluminum compounds as mordants, and their results have thrown much light upon the whole subject of mordanting. Sulpho-acetate of Alumina is obtained when an insufficient quantity of the acetate (lead or calcium) is added to decompose the alumina salt, and this forms the red liquor of trade. Ordinarily, the solutions have a dark-brown color and are characterized by a strong pyroligneous odor. The cotton-dyer and printer, especially the latter, make considerable use of this mordant, for reference to which, see p. 548. The remaining alumina compounds -viz., chloride, nitrate, hyposulphite, oxalate, etc.-are but little used,

Iron Mordants.—Like tin, iron is employed in two states of oxida tion,—ferrous and ferric. Ferrous Sulphate (FeSO<sub>4</sub>.7H<sub>2</sub>O), Copperas or Green Vitrol, occurs as a by-product from several chemical processes and is much used in cotton-dyeing, and in the preparation of iron mordants. Ferrous Acctate, also called Pyrolignite of Iron and Black iron Liquor, is manufactured similarly to the acetate of alumina, or by dissolving scrap-iron in crude acetic acid. It is applied in the same general manner, and to the same fibres, as the alumina compound. The remaining iron mordants are the Nitrates and the Nitro-sulphates. The former are obtained by dissolving scrap-iron in nitric acid to the proper degree of saturation, and the latter, by treating copperas with nitric acid; as an iron mordant for black on silks and as a weighting agen for black silks, this latter is probably the best, from the fact that the iron exists in both states of oxidization.

Chromium Mordants comprise among the most important Bichromate of Potash and Bichromate of Soda, both being products obtained from chromite. The former is well crystallized, the latter is quite deliques cent, frequently becoming fluid; in price it is cheaper than the potasl salt, and yields the same results. It is a valuable wool mordant, and i also much used as an oxidizing agent. Chrome Alum (Potassiun Chromium Sulphate) is a residue from the manufacture of alizarin, and is employed as the basis for producing many of the chromium mordants Chromium Acctate is obtained by double decomposition of lead acetat and chromium sulphate, and in commerce it is found of about 30° Tw (specific gravity 1.15). It is used in printing. Other compounds used are the chloride, sulphate-acetate, and alkaline chromhydroxide solution

Copper Mordants are well represented by the sulphate (blue-stone and the nitrate. Sulphate of Copper is used in dyeing blacks, mostly in conjunction with other mordants, and, owing to its cheapness, is used for the production of nearly all the copper compounds. Nitrate of Copper is easily prepared by dissolving scrap-copper, not brass (a free from lead and solder as possible), in nitric acid, and diluting to 1.4 specific gravity. In cold weather good crystals are obtained, but they absorb moisture very rapidly. The sulphide and acetate find little application except in special cases.

Antimony Mordants.—Tartar Emetic (Antimonial Potassium Tartate) is the best known of this group, and is much used for fixing tanni in cotton-dycing. Oxychloride of Antimony is another form, used for the same purpose. These products have been practically displaced by the double fluorides of antimony and potassium and of sodium which have been brought on the market as more convenient and desirable. The are well crystallized, easily soluble, and cheaper. The mode of application is the same as for other antimony salts.

Other mordants besides those above mentioned are used, but not extensively, and enough has been said to indicate their general natur under the operations of dyeing the special uses to which they are applicable will be mentioned.

(b) Mordants of Organic Origin.—Tannin (Tannic Acid) is no produced in large quantities of exceptional purity for use in the ar

and offers to the dyer a convenient mordant in place of many tanninyielding substances, which, however, still hold their position on account of other properties. Tannin is much used by the cotton-dyer, and is applied generally in two ways: first, by steeping, and, second, by pad-For silk, tannin is extensively used in the production of blacks, and also for weighting. Catechu, or Cutch (see p. 497), is used in a similar manner to tannin, for the production of browns, drabs, blacks, and other shades, in combination with bichromate of potash, copper, iron, etc. Catechu is bought in mats weighing about one hundred and fifty pounds, and also as "cutch extract," or "prepared cutch," made by dissolving the crude cutch, straining from sticks, stone, etc., and evaporating to about 51° Tw. It is used for wool and for silk. Sumach (Shumach) is used in the dye-house in the ground state, and as an extract, which is, in some instances, grossly adulterated. Nutgalls, rich in tannin, find extensive application both in dyeing and printing, especially when light shades are to be fixed. They occur whole, "crushed," and as an extract, which comes usually of two qualities. Myrobalans, kino, divi-divi (see pp. 359 and 360), etc., are also employed.

D. Dyeing.—The apparatus used by the dyer consists of vats, kettles, cisterns, etc., which are ordinarily constructed of wood, although they may be also of copper or similar metal, and even Their capacity, in case of woollen yarn, is such that they can conveniently accommodate a hundred pounds of material, although the sizes vary according to circumstances. Wooden kettles are heated by a copper steam-coil inside and on the bottom, and are provided with a water-supply pipe, and a lifting plug-valve for emptying. Metal kettles are preferably heated with steam by a coil or double bottom. The shapes of the vat or kettle vary with the material to be dyed. For cotton, wool, and silk yarns they are mostly rectangular, and of varying depth, for loose material, mostly circular; in the case of indigo-vats for yarns, they are wine-pipes stood on end; this gives a great depth of liquid with a minimum of exposure. In hand-dyeing, the yarn is hung, and worked on sticks laid across the top of the kettles; piece-goods are worked by means of a movable winch. Loose material is dyed as such in circular tubs, warps are passed over a series of rollers immersed in the dye-liquor, and then between squeezing or nipping rollers. Machine or apparatus dyeing is rapidly gaining in favor. Two general systems are in use: (1) Pack system, where the material is tightly packed in a vessel and the dye-color forced through it, and (2) Loose system, where the material is moved through the dye-liquor.

Of primary importance in successful dyeing is a regular supply of pure water, and in the absence of this, various means must be resorted to to purify the water at hand, which may be contaminated with sewage, which may not render it unfit for use, or else it may contain *lime* or magnesia, usually as bicarbonates, which are soluble, or it may have sulphates or chlorides. Iron (when present it is as a bicarbonate) is very objectionable, and, for some operations, prevents the use of the water. Water which has flowed through limestone regions will in-

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variably be hard from the lime dissolved, and that which flows or is pumped from granitic regions will be soft, due to the absence of lime, etc. In the event of water having suspended matter, this can be easily removed by suitable filtration, but if other impurities are present, chemical purification should be resorted to. A hard water is one which has bicarbonate of lime or magnesia dissolved, this solution being really a dissolving of carbonate of lime in carbonic acid contained in the water; besides the above, it may contain in solution sulphates of lime or magnesia. A water containing no sulphates, if boiled, would lose its hardness by the bicarbonate splitting off into carbonic acid gas and carbonate of lime or magnesia, which would be precipitated (temporary hardness); if sulphates were present, the boiling would have no effect on them (permanent hardness). A soft water is one containing no such impurities.

Chemical Purification for water embraces several processes, notably Dr. Clark's: decomposing the bicarbonate with a clear solution of calcium hydroxide, by this means the excess of carbon dioxide is combined with the lime added, which is precipitated and removed by settling. Only the temporary hardness is removed. The Porter-Clark process is similar to the above, with the exception that the precipitates are removed by the water being passed through a filter-press. Caustic Soda is also used as a purifying agent, which removes both the temporary and permanent hardness. The water will then be slightly alkaline. Alum and sulphate of alumina are extensively used in water purification for dyeing purposes. The alumina compound, if added to a water in suitable quantity, is completely eliminated by combining and separating with the impurities.

Solution of Coal-tar Colors requires a little care, because if imperfectly done the yarn or fabric will be spotted or striped: effects exceedingly difficult to remove. The colors are dissolved readily in warm water; some may require almost a boiling temperature, while others are injured when highly heated. They ought never be over a direct fire. In all cases it is well to strain through felt.

Cotton-dycing.—Two operations are necessary, mordanting and dyeing, except in indigo-dycing, where no mordant is required, and in the application of the substantive and primuline colors. In the case of raw slock, the operations are conducted in large circular or rectangular vats, heated as previously described, and provided with the necessary inlets and outlets for water, the outlet being covered with a gauze screen in order to keep the loose material from stopping it up. The material is "poled" or worked by long-handled rakes or by mechanical means. The washing can be done in a similar apparatus, or in one similar to a wool-scouring machine. For yarns, besides the open kettles mentioned on the preceding page, many mechanical devices are in use, and are well suited where large quantities of material are to be worked to one shade, but in cases where different shades are to be produced, hand-dycing cannot be excelled. For warps, the apparatus referred to on page 523 is used; it can be made with two or more kettles, so that the warp can

pass through two or more different solutions. This arrangement is admirable for mordanting, dyeing, and washing, or in the event of using the primuline colors, requiring rapid treatment. The several baths can be maintained at different temperatures.

Cloth-dyeing Machinery.—The vats are either iron frames and wood or all wood, in some places small enough to stand on the floor of the dye-house, in others they must be sunk below that level, in all cases surmounted with a hand or power winch for working the pieces. Drying is accomplished by wringing out the yarn, centrifugating, and hanging on wooden sticks in a "dry-room," or in the case of piece-goods, squeezing through rollers, centrifugating, and carefully arranging on sticks as above.

Application of the Natural Coloring Matters.-Indigo, including synthetic indigo.—This dye is always applied in the cold, and by any of the several "vats" now known, among which the lime and copperas may be mentioned. This vat, or series (usually ten), is made up in various proportions, the amount of ground indigo ranging from thirty to thirty-eight pounds, copperas, fifty to eighty-five, lime, eighty to ninety. The vats being filled with water, the lime is added, followed by the ground indigo and the copperas, raking the whole up occasionally until the indigo has been reduced, which is known by the olive-colored appearance of the liquid. A good working vat is known by peculiar blue streaks or veins which appear when it is raked. The dyeing is performed by dipping the wetted yarns in the oldest (weakest) vat, then squeezed out, placed aside to oxidize, and passed through the next, and so on until the proper depth of shade is reached, the whole operation being conducted systematically. The lime which is precipitated on the varn is removed by means of a weak acid and washing. Piece-goods are dyed in a similar solution by fastening the material to a large frame, which is dipped and re-dipped until the proper shade is obtained, or, in case of warps, also by passing over immersed rollers in a large vat, and finally over rollers exposed to the atmosphere; this is particularly suited for light shades.

Zinc-powder is much used in indigo-dyeing, supplanting copperas; for forty pounds of indigo about twenty pounds of zinc-dust are used. This vat is more economical than the preceding. Other vats are also employed,—viz., hydrosulphite, German soda vat, urine, etc., but those detailed indicate sufficiently the character of the operation.

Logwood.—This dye-wood is used in the form of liquid or solid extracts, and as chips, and mainly for the production of blacks. The cotton is mordanted in a cold solution of acetate or nitrate of iron, squeezed, and the iron precipitated on the fibre by passing through a solution of carbonate of soda, and boiled in the logwood-bath; or the cotton is allowed to steep in a solution of tannin (sumach, galls, etc.) for several hours, then worked in dilute iron solutions as above,—this produces a tannate of iron,—followed by a passage through weak lime-water, and dye in a separate kettle. Acetate of alumina can be used with the iron, somewhat modifying the shade. A "chrome black" can be ob-

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tained by dyeing in a single bath of bichromate of potash, hydrochloric acid, and logwood; many modifications of this process are known. Gray shades can be obtained by first working in logwood, and afterwards in the copperas or bichromate of potash baths.

Of the red dye-woods little need be said, as they are now but seldom used; their coloring matters are fixed in the usual manner with tin, alumina, or iron mordants. Of the yellows, Quercitron Bark and Fustic are the most important; the former, used chiefly as an extract, is available for the production of greens, etc., in combination with other coloring matters. Fustic is used to shade logwood black. Turmeric is no longer used in dyeing.

Application of the Artificial Coloring Matters to Cotton.\*—In this section only the individual colors will be referred to, any attempt to discuss the production of shades by compounding would be beyond the scope of this publication.

Fuchsine is dyed upon tannin-prepared cotton, or upon cotton that has been worked in small quantities at a time in a bath of ten per cent. of neutral soap or Turkey-red oil, followed by an immersion in a warm bath of two hundred and fifty gallons water and one gallon acetate of alumina (9° Tw.). Work half an hour, wash, pass through a soapbath for fifteen minutes, wash, squeeze, and dye. The color is added in successive portions until the required shade is obtained. Safranine is dyed upon a tannin mordant, or the tanned material is worked in a 3° Tw. bath of stannous chloride for an hour, washed, and passed through a two per cent. soap solution, and dyed at 140° F. Methyl and allied Violets can be dyed upon tannin as above, or pass the untanned cotton through a one per cent. olive-oil bath, squeeze, and dye at 100° F., or with the assistance of acetate of tin, or with alum and soda. The basic greens, including Victoria Green, Methyl Green, Brilliant Green, etc., are easily dyed upon cotton in the ordinary manner with a little (.5 per cent.) acetic acid.

The *Eosins*, with *Phloxin*, etc., are dyed in several ways: first, by passing the cotton through a two per cent. soap-bath, followed by an immersion for two hours in from two to three per cent. acetate of lead, washing well, and dyeing, cold, with a little acetic acid; or, second, by working in a dye-bath with eight to ten per cent. sulphate of soda, or the cotton can be worked in 5° Tw. bath of stannate of soda for an hour, worked for thirty minutes in a ten per cent. alum solution, rinsed, and dyed cold. *Rhodamin* is dyed on acetate of alumina exactly as for fuchsine. *Brilliant*, *Cotton*, and *Soluble Blucs*. The cotton is tanned and dyed with five per cent. alum and one per cent. soda; or the tanned cotton can be worked in a 3° Tw. stannous-chloride bath for an hour, rinsed, and dyed at 150° F. If light shades are to be produced, work the cotton in a five per cent. soap-bath for an hour, squeeze, and work in a three per cent. tannin-bath, wring out, and dye with the assistance

<sup>\*</sup>Reference has been made in the preparation of this and subsequent sections on its application to several of the published trade circulars issued by the coaltar color manufacturers, and also to information from private sources.

of tartaric acid and alum. Victoria Blue. Cotton is mordanted with tannin; dye with one per cent. acetate of alumina. Methylcne Blue. This is an exceedingly valuable color to the cotton-dyer, as with it he can produce indigo shades. The cotton is mordanted with twenty-five per cent, sumach at 160° F. Give several turns, and allow to steep ten hours, wring out, and work for twenty minutes in two and onehalf per cent. tartar emetic, wash, and dye in a bath prepared with acetic acid (three per cent.) at 75° F., gradually raising the temperature to 160° F. Crocëin Scarlets are dyed on cotton by working the untanned varn in stannate of soda, wring, and pass for half an hour through sulphate of alumina, rinse, and dye. Cotton can also be dyed by passing first through stannic chloride, and then through acetate of alumina. Dve cold, or dve direct, with sulphate of alumina. Auramin. of considerable value, is dyed in the same manner as methylene blue. Bismarck Brown and Chrysöidine. Dye same as safranine; temperature 100° F. Induline and Nigrosine. Dye in same manner as for the cotton blues. Paraphenylene Blue is dyed upon tin or antimony, and The shades produced are very dark, and extremely fast; treated with bichromate of potash, the shade closely imitates, and is faster than, indigo. The substantive colors of the Congo and parallel groups are exceedingly valuable, for the reason that they are easily dved upon unmordanted cotton, and that they are of exceptional fast-The several Congos. Benzo- and Delta-purpurin, and Rosazarin. are dyed with two and one-half per cent. soap and ten per cent. sulphate of soda, or phosphate of soda, boil for one hour. Hessian Purple is dved at a boil for half an hour with ten per cent. common salt, followed by a passage through dilute soda. Chrysamin is dyed with ten per cent. sulphate of soda and two and one-half per cent. soap at a boil. Hessian Yellow is dyed with ten per cent. of salt and a little Turkey-red oil. Brilliant Yellow and Chrysophenin are dyed with ten per cent. salt and two per cent. oxalic acid, work half an hour, squeeze, rinse, and Azo Blue, and Benzoazimine, Heliotrope, etc., are dyed with ten per cent. sulphate or phosphate of soda and two and one-half pounds of soap, let stand, and skim the surface, add the dye, boil, and put in the yarn, and work for an hour, boiling, rinse the yarn, and dry at as low a temperature as possible. Indigo shades from Benzoazimine are obtained as above, but for every one hundred parts of color add three parts Chrysamin. All the substantive dves act as mordants for a very large number of other colors, no other fixing agent being required. Diazotized and developed colors for cotton, of which primuline is the type are dyed in the usual way for a substantive color, then "diazotized "in a bath of nitrite of soda and a mineral acid, and afterwards "developed" by passing through a bath containing a developer, e.g., β-naphthol, which develops and fixes the colors. Dark blues and blacks are largely dyed by this process specially for hosiery, on account of the fastness. (See p. 541.)

The important group of sulphur colors dye cotton various shades, the most important being the blacks, blues including indigo shades, cutch shades and olives. Cotton is dyed from alkaline dye baths prepared with sodium sulphide, common salt, and the necessary color. The shades are noted for their fastness except to chlorine.

Another important group of cotton colors are the so-called "va dyes" which dye cotton from baths containing the coloring matter is a reduced state, similar to indigo. The range of shades is very extensive, possessing very good fastness to general influences, including chlorine.

Aniline Black.—This color is produced directly upon the fibre dur ing the dyeing by means of aniline oil in the presence of oxidizing agents; to obtain good results it is necessary that the oil used should b as pure as possible. Two methods are in general use, -warm (Grawit patent) and the cold. In the former method, two thousand four hun dred litres of water, thirty-two kilos. hydrochloric acid, sixteen kilos bichromate of potash, and eight kilos, aniline oil are taken. and aniline are each diluted with water and carefully mixed, the solu tion thus obtained being added to the main volume of water. The bi chromate of potash is previously dissolved and added after the aniline Immerse the cotton, and work for three-quarters of an hour in the cold and then gradually raise the temperature to 60° or 70° C. In th cold method take eighteen kilos. hydrochloric acid, eight to ten kilos aniline oil, twenty kilos. sulphuric acid, 66° Bé., fourteen to twenty kilos, bichromate of potash, and ten kilos, copperas. This bath is mad up similarly to the previous one, with the exception that much les water is used. Aniline salts in solid form are often used instead o aniline oil and acid. The yarn is worked in one-half of the material for an hour or so, after which the remainder is added, and the operation carried on for about one and a half hours longer, followed by a wash ing, and a boiling in a soap solution. In either case, the cotton after dyeing is subjected to a further oxidization with bichromate of potast copperas, and sulphuric acid,—this having a tendency to prevent greer ing. Chlorate of soda is used considerably as an oxidizing agent in th dye-bath. Vanadium chloride, or vanadate of ammonia, has bee recommended to be used with a chlorate in place of bichromate c potash; the proportion of the vanadium salt being to the displace bichromate as 1: 4000. Another method is to produce the aniline blac in powder form, purify it, liberate the base, which is dissolved in su phuric acid, poured into water, and the precipitate formed thereby di solved in caustic soda. This is reduced as in the case of indigo, an dved in a similar manner.

Alizarin-dyeing, Turkey-red Process.—J. J. Hummel, in his "Dy ing of Textile Fabrics," 1886, p. 427, et seq., details the emulsion process which need not be described here. It may be stated, however, the beautiful results have been obtained from its use; the yarn pass through fourteen operations, as follows: boiling in soda and dryin worked in an emulsion of oil, dung, and carbonate of soda; passe through the previous process twice again; worked four times in carbonate of soda, steeped in water, and in carbonate of soda, sumache

mordanted with alumina, dyed with alizarin (ten per cent.), sumach, and blood, cleared with carbonate of soda, final clearing with soap and tin crystals. To finish the dyeing requires about three weeks, but a real Turkey-red is produced. Except for some grades of goods, it is doubtful whether such a lengthy process would be profitable.

The following scheme of a process represents the type of a reasonably short one; it is well to remember that it can be modified to a considerable extent without altering its product. It is used in several establishments essentially as given. Boil the cotton for two hours in a 1.04 specific gravity solution of caustic soda, wash well in water, dry, and work in seven to ten per cent. solution of Turkey-red oil, squeeze, dry at about 115° to 120° F., steam in a chest, mordant with acetate of alumina (red liquor) at 80° Tw., and dry as before; work for an hour in a hot bath of five pounds of dung and eight to ten pounds of chalk, followed by a good wash, and pass to the dye-bath, made up of eight per cent. of alizarin, two per cent. Turkey-red oil, and about one per cent. of ground sumach, or equivalent in pure extract. Enter cold, and slowly

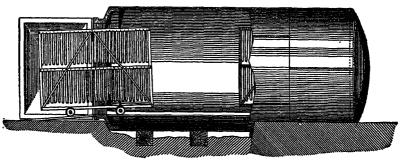


Fig. 120.

increase the temperature to and maintain it at 160° F. for over half an hour. Dry, and steam in the chest as above. The final operation is a

soaping with carbonate of soda and stannous chloride as in the above

emulsion process.

An almost unlimited number of processes could be given, but it is hardly necessary, the principle remaining the same in every case. For full information reference is made to Hummel, Sansone, and Knecht, Rawson, and Löwenthal. The apparatus used for alizarin-dyeing is not special, with the exception of the machines for "padding," the material to be dyed with the oils and for working in the liquors; the most important is the steam-chest, which is essentially a large cylindrical wrought-iron drum with cast ends, one of which is provided with a well-closing door. The chest, or *steamer*, is provided with a steam-supply pipe, gauge, and safety-valve. The yarn or cloth is hung on sticks supported on rods inside, or, as shown in Fig. 120, mounted on iron carriages. Some chests are so built that the yarn contained can be turned while closed and with the steam pressure on, which seldom exceeds four or five pounds.

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Ingrain Red, a color obtained from primuline or polychromine, is for some purposes a perfect substitute for Turkey-red, being fast to light, soap, and acids. Primuline is dissolved in warm water, common salt or sulphate of soda added, and the yarn worked in the bath until a good full yellow is obtained, when the material is washed, and immersed in a cold solution of nitrite of soda slightly acidulated with either hydrochloric or sulphuric acid, this causes a diazotizing of the yellow color, with the production of an unstable orange shade; the yarn is lifted out, washed rapidly, and at once dipped in a warm solution of β-naphthol in caustic soda, when a deep-red color is developed. The yarn is worked for a while, and afterwards well washed in water. phenol or resorcin is substituted for the \beta-naphthol, a fast yellow or orange color, respectively, will be obtained. The diazotized yarn is very sensitive to the light: if it is not in a reasonable time developed, no color will be obtained; this fact is at the present time experimented upon with a view to its possible use in photography.

A more recent and still better substitute for Turkey-red is the azopara-nitraniline obtained by diazotizing para-nitraniline C and developing with  $\beta$ -naphthol and red developer C. The cotton yarn is preferably first impregnated with the caustic soda solution of the developer, made with the addition of castor-oil soap, and then put in the diazotized solution.

Linen.—The uses to which fabrics made of this fibre are put demand colors that shall be fast to washing, light, and air; this requirement being satisfied by alizarin and indigo. The coal-tar colors, as a rule, are not applied, although they can be by treating the fibre in the same manner as cotton.

Jute, owing to its peculiar chemical structure, does not require any mordanting; all basic colors can be applied by simply boiling in a neutral bath. Some scarlets and a few of the acid colors are fixed with the assistance of a little acetic acid in the dye-bath, sometimes with a little sulphuric acid and alum.

Wool-dyeing.—Raw wool is dyed in the same manner as raw cotton, in open kettles, or in machines made for the purpose. Woollen yarns and cloth are similar in their manipulation to cotton, the apparatus being in both cases nearly the same. Dyeing-machines for carpet yarns are coming slowly into use, several forms being capable of handling a large quantity in comparison with hand labor.

Some classes of goods, i.e., plushes, have cotton backs,—these being previously dyed in the hank and warp and then woven,—the face, or pile, is afterwards dyed in proper shade, care being taken to select such colors as will have no modifying effect upon the cotton color. For this purpose cottons dyed with aniline black, indigo, or alizarin are best suited.

Natural Coloring Matters applied to Wool.—Indigo, as extract, is now but little employed for dyeing wool on account of its fugitiveness, when now used it is only for its cheapness. If other coloring matters are to be used in connection with the above for the production of com-

pound shades, a neutral extract had better be used, and the dyeing done without the use of acid. Wool is dyed in a vat, where exceptionally fast and full shades are demanded, especially for army cloth. Loose wool is dyed in the so-called fermentation-vat, the wool being kept below the surface of the liquor, worked about by means of long rakes for a sufficient time, and taken out and put in large cord bags, or placed upon rope screens to drain and oxidize. It is finally dipped in very dilute acid to remove soluble impurities, well washed, and dried. Woollen yarn is worked in vats exactly as in the case of cotton. Cloth is worked in the vat below the surface of the liquid, by means of poles with hooks. The best indigo-dyed cloth is that made from wool which has been previously dyed in the raw state,—dyed in the wool.

Logwood.—This dyestuff is the real base of the blacks upon wool, the most generally followed method being with bichromate of potash as a mordant. Boil the wool in a bath of three per cent. bichromate and one per cent. sulphuric acid for an hour, lift out, rinse, and boil in a bath (made with a decoction of about forty per cent. chipped logwood) for an hour, lift the wool, and add a little extract of fustic, continue the boiling for a half-hour. Frequently blacks of the anthracene groups are used in combination with logwood to give increased fastness. To prevent a "greening," or development of greenish tinge on exposure of the goods to the light, a coal-tar color, such as "cloth red," is dyed on first, so as to neutralize the effect of the green shade which may form. For cheap work "one-dip blacks" are used,—these consist chiefly of a mixture of logwood and a mineral mordant, iron or copper. Wool can be mordanted with copperas, copper, and cream of tartar, etc., followed by dyeing in the logwood, or it can be worked in the logwood first, followed by a "development" in a bath of ferrous sulphate of iron and copper.

Logwood Blue, for some kinds of work, is an excellent substitute for indigo, full shades being obtained by direct dyeing, or by dyeing upon a light indigo bottom. Hummel gives the following method. Mordant the wool for one to one and a half hours at 100° C. with four per cent. of aluminum sulphate, four to five per cent. of cream of tartar; wash well, and dye in a separate bath for one to one and a half hours at 100° C., with fifteen to thirty per cent. of logwood and two to three per cent. of chalk. The addition of a little alizarin or tin crystals to the bath at the termination of the dyeing will cause the appearance of "bloom," peculiar to indigo.

The red woods are fast losing ground, although before the introduction of the artificial scarlets and cardinals they were much used. Madder, likewise, has been superseded by artificial alizarin. Wool was mordanted for browns with bichromate of potash as for logwood; for reds, mordant with alum, or sulphate of alumina, with cream of tartar (argols), and boil. Tin crystals and tartar produce a reddish-yellow. These colors were not brilliant, but the value of them depended upon their fastness. The use of Cochineal is mainly for the scarlets obtained therefrom. The wool is mordanted with tin crystals and cream of tar-

tar, washed, and dyed in a bath with five to ten per cent. of cochineal (ground) for an hour. Another method is to boil the unmordanted wool in a bath of cochineal, tin crystals, and potassium oxalate for an hour. For scarlets with a bluish cast (crimsons) the wool is mordanted with aluminum sulphate and cream of tartar, or the wool can be mordanted in a bath containing tin crystals, tartar, and aluminum sulphate, followed by the dyeing in a separate bath. Copper, or iron, as a mordant will produce dark shades, and as impurities in the dye-baths will have a saddening effect upon the color obtained. Fustic is largely used in wool-dyeing, chiefly, however, in combination with other colors,i.e., indigo extract to produce greens, olives, sages, etc., and always upon mordanted wool, using tin crystals, sulphate of alumina, bichromate of potash, iron, and copper. Quercitron Bark is used for the same purpose as fustic and under the same conditions. Flavin, a production of the latter, is used in the same manner, its chief advantage is that it is much more concentrated. Archil (Orchil) as "extract," liquor, or paste is extensively used in the dyeing of carpet yarns; it is applied by simply boiling the yarn in a bath with the color, sulphuric acid, and sulphate of soda. It is exceedingly difficult to remove from yarn once dyed with it; a process which will economically accomplish this is much sought after by manufacturers.

Application of the Coal-tar Colors.—As a general rule, it may be stated that nearly all the soluble artificial colors can be dyed upon wool without any special treatment, by boiling in a bath with ten per cent. of sulphate of soda and two to four cent. of sulphuric acid. A few exceptions may be given: Alkali Blue (Nicholson's Blue). The color is dissolved in carbonate of soda, poured into the dye-bath, the wool entered, and the temperature raised to the boil, keep boiling for a while, lift, rinse well, and immerse in a bath of very dilute sulphuric acid, when the color will be at once developed. The Violets (Hofmann's, etc.) are dved neutral, or with a little soap. Methyl Green is applied to wool with borax, after having been mordanted with hyposulphite of soda. and hydrochloric acid. Auramine is dyed both neutral and acid. The Indulines are dved neutral, and then boiled in dilute sulphuric Gallëin and Carulëin are dyed upon wool mordanted with potassium bichromate and a small quantity of acetic acid. The application of Alizarin to wool is exactly as for madder, the general mordant being sulphate of alumina and tartar for reds; tin crystals and tartar for orange; potassium bichromate and sulphuric acid for red-browns; iron and tartar yield violet; and copper, shades of brown. The addition of a little lime to the dye-bath is necessary in case none is naturally present in the water.

Nitro-alizarin (Alizarin Orange) produces with several metallic mordants, applied as above, a range of shades, which have not reached commercial importance. Alizarin Blue is dyed upon a chromium mordant, and yields a durable blue, of some value,—for wool, the price of the dye is against it.

Alizarin blues, such as Alizarin Blue H R, which are made by com-

bining alizarin or a derivative of the same with a base, such as aniline, give various fast shades, and are dyed nearly the same as the older alizarin blue and alizarin blue S, except that the bath may be exhausted with very little or no acid.

The constant tendency to do away with the mordanting processes for wool dyeing has caused the development of certain groups of dyestuffs, which yield shades of extreme fastness, and which are produced by dyeing the wool in the presence of the chrome salt, or by dyeing first and "fixing" the color by adding the chrome to the extracted dye baths, or after chroming in a separate dye bath. It is instructive to note that some of the dyes which produce such shades on wool are old and well known cotton substantive dyes.

The *mineral* colors are dyed upon fibres through the decomposition of metallic salts, for example, to dye *Prussian Blue*, the wool is worked in a bath of red prussiate of potash and sulphuric acid, and gradually brought to a boil, squeezed, rinsed, and dried.

Silk-dyeing.—Silk has a great affinity for the coal-tar colors, with which it can be dyed without any mordant, although it is customary to employ a soap-bath (boiled-off liquor) with or without the addition of a weak acid, usually acetic. If soap is not used the colors will appear streaky or spotted. For ribbons, fancy dress goods, plushes, etc., the above colors are solely employed, with the possible exception now and then of recourse to some natural coloring matter, the use of the latter being almost restricted to logwood for blacks and modified shades, including browns. Silk is dyed in skeins or hanks, warps, or pieces, this latter including plushes. The machinery is of the simplest kind, embracing the kettles, with and without winches, washing-machines, etc., and need not be especially described.

Silk is not dyed with indigo (vat process), but indigo shades are obtained by using indigo-carmine. Black is obtained by several processes. Work the silk in acetate of iron and wash, then in a warm soap solution, followed by an immersion in ferrocyanide of potash, washed, and worked again in the iron-bath, rinsed well, and steeped in a solution of catechu or gambir for ten or twelve hours and washed. This preliminary process is necessary in order to insure a good result if systematically carried out and not forced. The material is dyed in a logwood decoction containing soap.

To obtain heavily weighted goods, for blacks, the process of dipping in iron solution and then in tannin-containing liquors is often repeated several times. A method giving excellent results, and which is considerably used, is as follows: Wash the goods, and pass through a bath of nitrosulphate of iron, wash, and then through a solution of carbonate of soda. These two operations are repeated several times, each time causing the precipitation of more iron upon the fibre, and consequently "weighting" the silk. Work for some time in a bath of ferroprussiate of potash and then in a bath of catechu, followed with a little "muriate of tin" or tin crystals, wash, and transfer to the logwood-bath, which may contain a little extract of fustic to modify the shade required,

then to a soap-bath. Every locality is not suited to black silk-dyeing on account of impurities in the water, careful purification of which is a special requisite. Seal plushes are dyed, first in a dye-bath in the ordinary manner, a dark-brown shade, followed by the application of a black, blue-black, or other color, in the form of a paste thickened with starch, gum, or other medium, the application of this being done on a machine provided with revolving brushes, and so regulated that only the tip or face of the piece of goods is coated. One important feature in plushes of this character, and also in other kinds of silk goods which have been heavily iron-mordanted, is that the natural lustre of the fibre is somewhat destroyed; this loss is supplied by means of a mixture of vegetable oils made into a paste with starch or other substance, applied as in the case of the tip, and steamed in an apparatus similar to that used for alizarin red (p. 540). The oil, usually a definite amount, is absorbed by the silk fibre under the influence of steam, imparting a permanent lustre. The goods, when removed from the steamer, are washed to remove the starch, excess of oil, etc., when they are ready for other operations.

"Dynamited" silk is silk weighted with stannic chloride (dynamite) and fixed with silicate and phosphate of soda, and for full fibres with sulphate of alumina. Weighting may be as high as 400 per cent.

A class of fabrics similar to plush, but with the pile of two or even three colors, much used for carriage-robes, etc., and dyed to imitate the skins of animals, are prepared in the following manner: The material (cotton in black with silk pile, the former previously dyed a fast color) is dyed, say a brown, in the ordinary manner; upon the fibre is then applied a discharge made of stannous chloride solution and permanganate of potash. This is so controlled that only one-half of the fibre is acted upon. When the effect is produced the excess is washed off, rinsed, dried, and, if necessary, a tip is applied, which only dyes the very face of the pile. In this manner three colors are obtained on each thread of the face. After treating as above, the whole may be dyed a very light shade, thereby producing modified effects.

The artificial coloring matters are applied to silk as previously stated. Nicholson's Blue (Alkali Blue) is applied as directed for wool, and seldom for the production of mixed shades. Picric Acid is much used for compounding, especially for greens, faster colors can be obtained by using naphthol yellow and indigo-carmine. The Eosins yield beautiful colors, and are applied in a soap-bath followed by a brightening in dilute acid. The Azo dyes are applied with a neutral soap-bath.

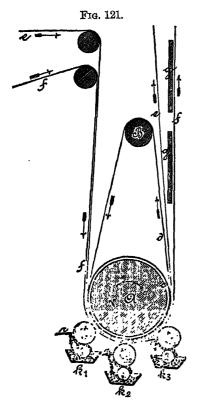
The use of Alizarin with silk is only in cases where fastness is of more importance than brilliant shades. Alizarin Black is being much used in dyeing mohair goods (astrachans), and is applied in the ordinary manner.

E. PRINTING TEXTILE FABRICS.—A brief outline of the more important "styles" in use is all that will be attempted in this section, from the fact that the subject is too extensive to enter into the details satisfactorily. The processes in general are conveniently divided into

two main groups, differing in the manner of applying the colors,—namely, Direct Printed Colors and Dyed Colors.

Direct Printing is done by mixing the desired color with the proper fixing agents and applying directly to the fabric by means of blocks engraved with the design, or in a machine provided with a cylinder upon which the design is likewise engraved; for each color to be applied a separate cylinder is needed. From the above it is obvious that the color so applied will appear only on those portions of the fabric brought in contact with the design.

Dyed Colors are obtained by printing different mordants upon the



cloth, as above, and fixing as for ordinary cloth, and then dyeing the whole, or, by printing upon the cloth resists, substances which will prevent the dye from becoming fixed at those places so printed, or, again, by dyeing the whole pieces first, and then producing patterns or designs by means of substances which will destroy the ground-color whenever brought in contact; these substances are called discharges. This broad definition is deemed sufficient for the purpose intended; the principle of each style will be apparent upon following the methods hereafter given.

The operations conducted in a print-works embrace as a preliminary bleaching, the details of which are referred to on p. 524. Then the preparation of the colors, which is always done in copper pans mounted in such a manner that they can be emptied easily, and that their contents can be boiled by steam, and cooled by water, facilities for this being done by means of steam and water trunnions connecting with the double bottom of each pan. From five to eight pans are supplied in a "bat-

tery," although it is often convenient to have one or more pans separately mounted, and without steam taps. The agitation of the contents is performed either by means of wooden paddles or, preferably, by mechanical agitation, which can be raised clear above the top of the pan, and without interfering with the working of the others. As the majority of colors used are made with either starch or flour for thickening, it is necessary, to insure good results, that they are strained or filtered; for this purpose it is well to have wooden frames made, over which is tacked brass or copper wire cloth (iron is inadmissible). The most important piece of apparatus is the printing-machine, an idea of

the construction and operation of which may be had from Fig. 121. A is a cylindrical "bowl" or drum, covered with several thicknesses of felt cloth, c; around this drum, and passing over a smaller one, B, is an endless band, d (full width of the machine); over this band, and acting as a guide to the fabric to be printed, is another band, e. which serves to keep d clean, being, in fact, a piece of cloth yet to be bleached and printed; the piece being printed is indicated by f. The means for applying the color are shown in the figure below the large drum,—viz., the printing rollers or engraved cylinders  $h_1$ ,  $h_2$ ,  $h_3$ , which are fed with color through coming in contact with the wooden rollers  $n_1$ ,  $n_2$ ,  $n_3$ , which dip in the color contained in the troughs  $k_1$ ,  $k_2$ ,  $k_3$ . Pressing against each of the rollers, h, is shown a small strip of metal, r, technically termed the "doctor," the purpose of which is to remove the excess of color from the face of the printing-rollers before they come in contact with the cloth. These "doctors" are best made of bronze or gun-metal, or some of the newer aluminum-copper alloys,—capable of better resisting weak acid. Before the cloth is printed upon it passes over a "lint doctor," the office of which is to remove any loose hair or fibres from the cloth. Printing-machines are built with any number of color boxes and rollers up to twelve or fourteen, each being for a separate color. Sansone mentions one for use with twenty colors. Great nicety is required in adjusting the machines in working to have no overlapping of colors or mordants,—perfect "registration" being sought.

For drying the printed goods revolving cylinders, or "cans" of large diameter, are used, or the goods are passed over heated plates, in no case allowing the printed face to come in contact with any part of the apparatus. Steaming follows to fix the colors, the apparatus being a steamer, as shown on p. 540, or one constructed of brick and iron, acting continuously, thereby turning out much more work than the former. The dyeing- and washing-machines are similar to those already described.

Mordants, Resists, Discharge, etc.—All the various substances used in printing must be applied in the form of pastes, the consistency of which must be such that whenever applied they will not run or spread, which impairs the sharpness of outline of the printed pattern. For the purpose the color-mixer has recourse to the starches and gums, the most important of which are corn or wheat starch, and flour, usually made up into ten per cent. pastes. The gums include gum arabic, dextrine (British gum), and tragacanth. The first is used in several degrees of consistency, from a fifty to a one hundred and fifty per cent. solution, dextrine the same, and the last in a ten per cent. paste. The proportions are by no means uniform, but they represent the average strengths used in the color house. Blood albumen is considerably used, large quantities being manufactured cheaply in Chicago and other Western localities. The mordants used embrace the acetates of alumina of various strengths, basic sulphate, and others of less importance. The acetates and nitrates of iron are the most prominent salts of this element, and of chromium there may be mentioned the acetates and nitrates; others, including salts of tin, calcium, manganese, are also used. Owing to the great number of recipes published for preparing mordants, as of the difficulty in selecting those which may be called representative only a few will be given of the more important.

Acetate of Alumina, or "Red Liquor" (Crookes) .-

Water	45	gallons.	45	gallons.
Alum	100	pounds.	200	pounds.
Acetate of lead	100	- "	200	- "
Soda crystals	10	66	10	66

Or the same result can be had by substituting acetate of calcium f the lead salt. In either case the alumina salt is dissolved in about ha the quantity of water, and the acetate in the remainder, when the tv solutions are mixed and allowed to settle, the precipitated lime or less sulphate being removed. The addition of soda is to neutralize any fracetic acid.

Acetate of Iron, or "Black Iron Liquor," can be obtained either I double decomposition as above, or by dissolving scrap-iron or precip tated oxide of iron in crude acid. In the former method sulphate iron and acetate of lead are used as follows: Water, forty pounds, suphate of iron, twenty-four pounds, acetate of lead, twenty-four pound Dissolve each separately, mix, and filter. The oxide of iron above me tioned is obtained by precipitating a solution of copperas with ar monia or soda, filtering and washing, and dissolving the moist precipate in ordinary acetic acid to make a twenty-five per cent. solution. In the event of using soda, much longer washing is required.

Nitrate of Iron is made as above; copperas and nitrate of lead beir used for the decompositions in equal proportions. Nitrates made I direct solution are obtained by several methods, the best being nitr acid nearly saturated with scrap-iron and diluted to about 80° T. Some of the so-called nitrates of iron are mixtures of sulphate ar nitrate of iron and some are composed entirely of sulphate of iron, whi others are waste liquors, such as are obtained by dissolving iron out "tin scrap" by means of sulphuric acid. Others may contain hydrehloric acid, with or without the addition of copperas. Chromium Actate is similarly prepared with chrome alum and lead acetate, or I precipitating chrome alum with an alkali, and dissolving the wash precipitate in acetic acid, or in nitric acid if the nitrate is wanted. Th latter mordant can be made by using lead nitrate and chrome alum.

The tin mordants are used to brighten the color with madder ar cochineal dyeing. The first is Stannous Chloride,  $SnCl_2 + 2H_2O$ . is made by dissolving tin in hydrochloric acid and evaporating the soltion. It is used somewhat in wool-dyeing, but more largely in calic printing. Stannic chloride,  $SnCl_4$ , is also used, and its combination wis sal ammoniac known as "Pink Salt," and Sodium Stannate, Na<sub>2</sub>SnC known as "Preparing Salt."

The principal styles of printing tissues are given in the followir scheme, condensed from a tabular view given in Sansone's exceller work on "Cotton-Printing."

PRINTED (DIRECT) COLORS.

- 1. Steam or Extract Styles.
  - (a) Coal-tar Colors.
    - Alizarin, Basic Aniline Colors, Acid Colors, and Neutral Azo Colors.
  - (b) Dycwood Extracts (natural organic coloring matters).

    Logwood, Quercitron Bark, Sapan and other Red Woods,
    Catechu, Annatto, Cochineal.
  - (c) Steam Mineral Colors.
- 2. Pigment Styles (fixed by albumen).
- 3. Oxidation Colors.
- 4. Direct Indigo-printing (alkaline styles).

DYED COLORS.

- 5. Alizarin Dycd Styles.
- 6. Turkey-red Styles.
- 7. Indigo Styles.
- 8. Manganese Bronze Styles.
- 1. Steam Styles.—Here the colors and proper mordants are mixed. and applied to the fabric in one operation, followed by air drying and steaming, or by immediate steaming, drying, and again steaming, the object in each case being to fix and develop the colors. Several conditions are to be noted in this style, chiefly the humidity of the steam, temperature, pressure, and the duration of the steaming, in order that the same shades may be again obtained with the same colors. Before being printed the cloth is passed through a solution of stannate of soda, also called "preparing salt," and then through sulphuric acid (1.005 to 1.015 specific gravity), washed, and dried. The colors best suited are the basic,—that is, those which form insoluble lakes with tannin in combination with a metal, and the general method of applying the same is given in the following extract from Sansone ("Printing"), p. 208: "A color is formed consisting of thickening, the solution of coloring matter, and acetic acid. The acetic acid is added in the preparation of the color in order to prevent the tannic acid from combining with the dyestuff; in other words, the acetic acid keeps both the coloring matter and the tannin in solution in the thickened color, and prevents their combining with each other; but when the color is printed and the cloth is dried and steamed, the acetic acid is expelled, and the coloring matter and the tannin then go into combination to form the insoluble colored lake. This lake, however, not being sufficiently fast to stand by itself, a metallic mordant is necessary to give additional fastness to the colors: for this reason the cloth, after printing, dyeing, and steaming, is passed into a solution containing tartar emetic." The antimony of which at once unites with the "tannate" of the color already on the fabric, thereby producing a more insoluble body. The steaming operation must be conducted with such a volume of steam that the acetic acid volatilized can be carried away, or else the colors may be injured. Of the colors employed may be mentioned the Fuchsines, Methyl Violets and Greens, Bismarck Brown, Naphthylene Blue, etc.

Alizarin, without exception, is the most important coloring matter used in cotton-printing, for which purpose the goods are previously treated with alizarin oil and dried. With alizarin in printing, as in dyeing, the color obtained depends upon the selection of the mordant, which can, however, be a mixture; for reds, alumina, with or without tin; purples, iron; browns, with either ferricyanide of potassium or acetate of iron, and acetate of alumina, or with chromium mordants. When the fabrics have been printed they are steamed for one or two hours, and passed through a heated chalk-bath, washed, and soaped. The following indicate the methods of preparing several colors:

#### Red. (Standard.)

Alizarin paste (fifteen per cent.)	6	pounds.
Starch paste		
Acetate of alumina (11° Bé.)	11/4	pints.
Acetate of lime (15° Bé.)	1	pint.
Nitrate of alumina (13° Bé.)		

#### Purple. (Standard.)

Alizarin Starch paste	
Acetate of iron (13° Bé.)	1 quart.
Acetate of lime (13° Bé.)	
Acetic acid	1 "

#### Brown. (Standard.)

Alizarin (fifteen per cent.)	4	pounds.
Starch paste	1	gallon.
Nitro-acetate of chromium (25° Bé.)	3	pounds
Acetate of lime (13° Bé.)	¼	pound.

Since the introduction of the alizarin greens and violets, their use in connection with chromium in cotton-printing has been most rapid.

Dye-woods, with the exception of logwood, have been nearly super-seded by the tar colors. The method of applying the color is nearly the same as for other steam colors,—viz., print, dry in the air, steam, and wash, and is made up with chromium as the mordant, and an oxidizing agent, with or without the presence of another coloring matter to modify the shade.

The following recipes illustrate the color as made for blacks:

## Steam Logwood Black. (Sansone.)

Water	1	gallon.
Acetic acid (6° Tw.)	1	"
Logwood extract (30° Tw.)	1	cc
Quercitron bark extract (30° Tw.)	2	pounds.
Starch	5	"
Dextrine	2.5	"
Olive oil		
Chlorate of potash or soda	.75	"
Boil, stir until cold, then add		
Acetate of chromium (20° Tw)	1	gallon.

#### Steam Logwood Black. (Sansone.)

Starch	6	pounds.
Flour	6	44
Acetic acid (6° Tw.)	2.5	gallons.
Logwood extract (20° Tw.)	3.5	cc
Acetate of iron (15° Tw.)	3.5	66
Olive oil	1.5	pounds.

Of the other natural coloring matters there may be mentioned Cochincal, applied with tin or alumina; Sapan, in the same manner, and Quercitron Bark, with alumina or chromium. Catechu, most used for browns, may be applied with acetate of chromium or with logwood and fuchsine

The Mineral Colors are to some extent made use of, their application depending upon the principle of double decomposition upon its fibre when subjected to steaming. The following examples will make the principle clear: Yellows are obtained by the decomposition of nitrate of lead and a soluble chromate, the insoluble chromate of lead ("chrome yellow") being formed. For Blues, both prussiates of potash are used. Brown is obtained by means of chloride of manganese and bichromate of potash.

- 2. Pigment Styles.—For this style effects are produced by means of insoluble color lakes and the mineral colors, which are fixed upon the cloth by steaming, the action of which coagulates the albumen with which the colors are invariably mixed for printing. The colors are generally supplied to the color-mixer in a dry condition, and include Ultramarine of various qualities, Vermilion (sulphide of mercury), the Chromates of Lead and Barium, Cadmium Yellow (cadmium sulphide), Chrome Green (oxide of chromium), the Ochres, yellow and red, and Lamp-black. A familiar example of this style is seen in cheap flags and decorative muslins.
- 3. Oxidation Colors.—The most important of this class is Aniline Black, and will be briefly outlined as follows: Aniline oil is made into a paste with a chlorate (soda generally) and a metallic salt, with the proper amount of starch paste. This is printed upon the fabric, "aged" for forty-eight hours, or passed through a "steam ager," then passed through a warm bath of bichromate of potash, washed well, and finally worked through a soap-bath. The metallic salt mentioned acts as a carrier of oxygen, and for the purpose vanadate of ammonium, sulphide of copper, bichromate of potash, etc., are used. For the preparation of the color paste the following methods are given:

1. Water		1	gallon.
Aniline salt		. 2	pounds.
Aniline oil	٠.	. 2	"
Starch		. 2	"
Dextrine		. 1/2	pound.

The paste is made first with the starch and dextrine, then the aniline is added.

2.	Chlorate of soda (8° Bé.) 1	gallon.
	Starch 2	pounds.
	Dextrine	pound.
	Chloride of ammonium½	"

These are made separately, but when wanted are mixed, and two pounds of *sulphide of copper* paste are added, and the whole well mixed and strained. (Crookes.)

The use of vanadium is shown by the following method (Sansone, "Printing," p. 275):

.

Water		0
Starch	11/2	pounds.
Dextrine	3/4	pound.
Boil, cool down to 120° F., then add		_
Aniline oil	11/2	pounds.
previously neutralized with		-
Hydrochloric acid (32° Tw.)	11/2	pounds.
Stir until cold, then add a cold solution of		-
Chlorate of soda	3/4	pound.
Boiling water	1	- 66
Before printing add further		
Vanadium solution	1/2	u
Print, dry not too hard, age two days, then pass through two	per	cent. solution of
bichromate of potash at 160° F., wash and soap.	•	

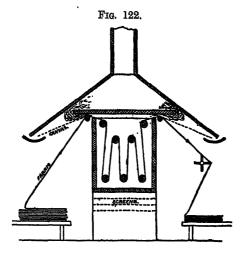
The vanadium solution is made with vanadate of ammonia, hydrochloric acid, glycerine, and water, and contains about .15 gramme per litre.

Other colors are produced by oxidation,—namely, Brown (with phenylendiamine, Sansone), by simply printing with a chlorate, drying, and steaming, Yellow, Grays, Olives, Blues, etc. To obtain white patterns on goods printed with aniline black, a "resist" or "reserve" is first applied of the desired pattern, consisting of white arsenic as the base, with caustic soda, and the proper thickening. For discharging the aniline black after it is printed, permanganate of potash is used; the goods are afterwards passed through a solution of oxalic acid.

4. Indigo-printing.—Indigo is printed upon cotton fabics in two ways, one of which is known as the "Glucose," and the other the "Reduced Indigo" Process. The former is carried out as follows: Indigo is finely ground, and made into a paste with water, to which is added caustic soda; this is now kept in a closed vessel in order to prevent as much as possible the absorption of carbonic oxide from the atmosphere. When used in printing, it is thickened with dextrine and starch; the following table (from Sansone, "Cotton-Printing," p. 284) showing the proportions used for several shades:

Light calcined starch	3	parts.	3	parts.	3	parts
Indian corn starch	11/2	- "	11/2	~ «c	11/2	- "
Water	33/4	"	33/4	66	3¾	46
Caustic soda lye (70° Tw.).	16	æ	28	"	40	66
Indigo paste	30	ec .	18	"	6	66

The cloth, before being printed upon, is worked through a twenty-five per cent. solution of glucose and dried. After printing, the cloth must be again dried and passed through an atmosphere of wet steam, in an apparatus shown in Fig. 122, to effect the reduction of the indigo, which now takes place. The cloth is now washed in water, being repeatedly, during the washing, exposed to the air, when the reduced indigo is oxidized and its real color appears. The reason for rapidly steaming is to act upon the caustic alkali while it is still in that state,



as if it should become carbonated through delay little reduction will take place. This method is employed in printing indigo upon alizarindyed goods and in other combinations with resists, etc.

The "Reduced Indigo Process" is based upon the fact that indigo, when finely ground and mixed with lime and thiosulphate of soda in suitable thickening agents, is reduced; if, with this reduced indigo paste, patterns are printed upon cotton fabrics, and then exposed to the air, the indigo is oxidized with a regeneration of the blue color. The pieces are then washed and dried.

Instead of using indigo in printing, one of the newer colors, *Immedial Blue*, is now very extensively used and printed with suitable mordants directly upon the goods.

5. Dyed Alizarin.—This process differs from all those previously mentioned in that the colors are produced by first printing upon the fabric the thickened mordants suited to alizarin, ageing, during which the mordants so printed are decomposed and more firmly fixed upon the cloth, dunging, an operation which removes the thickening no longer

discharges, which may or may not be made so as to yield colored patterns. The base is citric or tartaric acid, thickened with a suitable paste, and if for colors, containing a salt of lead if for a yellow discharge, or ferro-prussiate of potash for a blue discharge, or iron and logwood for a black discharge. After printing on the discharges, the goods are passed through a bath of bleaching-powder, well washed, and then, if lead has been printed on, passed through a bath of bichromate of potash, when chrome yellow will be produced. If the prussiate of potash has been printed, a blue color will be developed. Green is obtained by mixing both discharges first.

- 7. Indigo Styles are similar to the above; resists are printed on the cloth, which is then dyed in the vat in the ordinary manner, when, upon a removal of the resist by suitable means, white patterns are had upon a blue ground. By the system of discharges various colors may be put on by means of lead and other metallic salts. Vermilion is applied directly with albumen. For a discharge which has to be afterwards dyed red with alizarin, bromide of manganese and an aluminum salt are used.
- 8. Manganese Bronze Style, or Bistre Style.—This process has for its object the production of hydrated peroxide of manganese upon the fibre, and the subsequent printing of colors by means of discharges. The goods are worked in a solution of manganous chloride, dried, and worked in soda lye, washed and passed through a solution of chloride of lime until a brown color is produced. Wash, dry, and the goods are ready for printing. A discharge for white is made with muriate of tin (120° Tw.); for blue, yellow prussiate of potash with an organic acid; for yellow, a lead salt, developed with bichromate of potash. Green and black as in the previous style.

Woollen- and Silk-printing.—Wool, either as yarn or fabric, is generally printed with the tar colors, and according to the steam style previously described. The goods are dried after printing, steamed for one hour, and well washed. Silk is printed in the same style after being prepared by suitable agents, such as tin with or without an acid. Previous to being printed both silk and wool must be entirely free from grease. Silk warps for ribbon and veiling are often printed by hand blocks, and with aniline colors dissolved and thickened with Irish moss. After printing, the warps are simply air dried—being neither washed nor steamed. Such colors are not fast, but they are much used for so-called "Dresden" and "Persian effects."

The following table from Rupe's "Chemie der Natürlichen Farbstoffe" (Braunschweig, 1900) shows the artificial dye-colors which have replaced or are in practical use competing with the natural dyestuffs named:

NATURAL DYESTUFFS.	Is displaced for cotton.	Is displaced for wool and silk.
QUERCITRON	Mainly by substantive dye-colors:	Is not much used now, the different mordant coloring yellows having taken its place. In addition, Naphthol yellow S (H.), Tartræine, Quinoline yellow (H.).
Persian Berries	Are still much used in cotton-printing and in connection with tin salts. For direct printing compete: Auramine, Thicknein (O.), the latter exclusively for discharges; in addition, Chloramine yell Important are icylic acid azo colors, such as Alzarin yellow (H.), etc.	Little used for wool, For silk replaced by Tartrazine, Fulling yellow (C.), Naphthol yellow S (H.).
WELD	Alizarin yellow (H.), etc. Is hardly ever used for cotton.	Is little used for wool, but, on the other hand, largely for silk. Is v S, lling mine
Fustio		Is still much used in wool-dyeing, although the different yellows: Am G., Chrome yeuww (C. tr.), Moraant yellow (C. G.), Fulling yellow (H.), Azo yellow (H.), Fast yellow (H.), Altacrin yellow (H.). With wool the case is the same as
LOGWOOD	is still unreplaced. In cotton dyeing (for black) is about given up. For better goods is replaced by Aniline black, Diaminogen black the blacks: "ydiamine black" (C.), Direct de black, Immedial black (G. H.), and similar sulphated products.	while details. It is still used for dyeing, but is losing ground rapidly. The substitutes are: Naphthol and ck (C. G. H.), Diamond black (C.), Auzarın olack (G. H.), Anthracene black (C. G.), Azo acid black
Brazil-wood	For cotton scarcely used now, being replaced by the substantive dyeing reds: Diamine fast red F (C.),	and Also for wool and silk almost entirely replaced by Cloth red (C.), Wool red (C.), Acid fuchsine (G.), Fust red (H.), Indicate the cellin (G.); in indicate the cellin (G.); in indicate the cellin (G.); in indicate fast red (C.), Chromotrope (H.).
COCHINEAL	Auzuren reu (ri.).	Is still used somewhat for wool and silk, but is being displaced by vivid acid wool colors, such as Azocosin (G.), Chromazon red (G.), Palutine scurlet (H. C.), Brilliam crocein (H.), Brilliam (Cochineal (C.), and the different Ponceaux,
ARCHIL		etc.  H ntirely dissilk by the acid wool  ), Azocar- il substitute (C. G. H.), rubine (C.), Azo acid fuchsine (H.), Rosindu- tirope (H.),
Annatto	For cotton is replaced by the different artificial orange colors, as	wopo (11.).

3

NATURAL DYESTUFFS.	Is displaced for cotton.	Is displaced for wool and silk.
SAFFLOWER	Was first replaced for cotton by the Eosines, Phloxine (C. G.); later these were displaced by Rhodamine (C. G.), Erica (C.), Diamine rose (C.), Geranine (C.), Safranine (H.), etc.	
BERBERINE		Is not used for wool, but still somewhat for silk. Substitutes are the same as those mentioned for Weld.
CATEORU	still used for cotton, although a whole series of excellent substantive dyes have appeared. Especially have the Diamine colors, Benzo and Congo colors with supused, although the different Alizaria colors are seeking to displace it in part (C.).  Comunication of the colors of the colors are seeking to displace it in part (C.).  Comunication of the colors of the colors of the coloring and diazottzable blues of the Diamine, Diphenyl, and Benzo colors of related colors, which has recently appeared, seems to be among the most important substitutes. In calico-printing, Indigo has been in part replaced by the Synthetic indigo preparations and by the difficulty of the circular of the colors of the suppared, seems to be among the most important substitutes. In calico-printing, Indigo has been in part replaced by the Synthetic indigo preparations and by the difficulty of the circular of the colors of the colo	Still used for silk in combination with logwood in large amount without any competing products (C.). For weighting of silk.  On wool, is replaced on the one hand by Alizarin blue (C. G. H.), in cyanine by Sulphonocyl blue. However, the application of Indigo to wool still holds out relatively well.
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The communications upon which this table is based were from the firms of Leopold Casella & Co., of Frankfurt-am-Main (C.), Joh. Rud. Geigy & Co., of Basel (G.), and Farbwerke, vormals Meister, Lucius and Brüning, of Höchst (H.).

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## APPENDIX.

## I. The Metric System.

THE French metric system is based upon the idea of employing, as the unit of all measures, whether of length, capacity, or weight, a uniform unchangeable standard, adopted from nature, the multiples and subdivisions of which should follow in decimal progression. To obtain such a standard, the length of one-fourth part of the terrestrial meridian, extending from the equator to the pole, was ascertained. The tenmillionth part of this are was chosen as the unit of measures of length, and was denominated meter. The cube of the tenth part of the meter was taken as the unit of measures of capacity, and denominated liter. The weight of distilled water, at its greatest density, which this cube is capable of containing, was called kilogram, of which the thousandth part was adopted as the unit of weight, under the name of gram. The multiples of these measures, proceeding in a decimal progression, are distinguished by employing the prefixes, deca, hecto, kilo, and myria, taken from the Greek numerals; and the subdivisions, following the same order, by deci, centi, milli, from the Latin numerals. Since the introduction of this system it has been adopted by the principal nations of Europe, excepting (freat Britain, and in many of them its use is compulsory. It is in general use in France, Germany, Austria, Italy, Spain, Norway, Sweden, Netherlands, Switzerland, Greece and British India. It was legalized in Great Britain in 1864, and in the United States by an act of Congress in 1866.

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The meter, or unit of length, at 32°, = 39.370432 inches.
The liter, or unit of capacity, = 33.816 fluidounces. U. S.
The gram, or unit of weight, = 15.43234874 Troy grains.
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Upon this basis the following tables have been constructed:

#### MEASURES OF LENGTH.

		English inches.			English inches.
Millimeter (mm.)	_	.03937	Decameter (Dm.)	_	393.70432
Centimeter (cm.)		.39370	Hectometer (Hm.)	=	3937.04320
	_	3.93704	Kilometer (Km.)	-	39370.43200
Decimeter (dm.)	_	39.37043	Myriameter (Mm.)	2000	393704.32000
Meter (m.)		0 ±0 10.60	•		561

#### MEASURES OF CAPACITY.

English cubic inches.

Milliliter (ml.)		.061028	Decaliter (Dl.)	==	610.280000	
Centiliter (cl.)	=	.610280	Hectoliter (Hl.)	=	6102.800000	
Deciliter (dl.)	=	6.102800	Kiloliter (Kl.)	-	61028.000000	
Liter (l.)	===	61.028000	Myrialiter (Ml.)	=	610280.000000	
	•		OR THE CAME			
		MEASURES	OF WEIGHT.			
		Troy grains.			Troy grains.	
Milligram (mg.)	==	.0154	Decagram (Dg.)	_	154.3234	
Centigram (cg.)	200	.1543	Hectogram (Hg.)	=	1543.2348	
Decigram (dg.)	=	1.5432	Kilogram (Kg.)	=	15432.3487	
Gram (gm.)	-	15.4323	Myriagram (Mg.)	=	154323.4874	
Ú	топт	TATARNA WHEIGH	HTS AND MEASURES.			
1  kilometer = 109			1  foot = 0.3048  me			
or	0.621 statu	ite mile	1  yard = 0.9144  m	eter		
1 square meter =	10.764 squ	are feet	1  square foot = 0.0			
1 cubic meter = 5			1 cubic inch $= 16.$	38 <b>72</b> ∙c	ubic centimeters	
1  liter = 1  quart  s	and 🖠 gill T	J.S. measure	1 cubic foot $= 0.02$	2832 cı	ıbic meter	
or 1 pint and 3			1 pound avd. $= 45$	3.5925	grams	

#### or 0.03381 fluidounce 1 hectoliter = 26.4 U.S. gallons or 22.01 Imperial gallons

1 cubic centimeter = .061 cubic inch

1 kilogram = 2.204 lbs. avd.or 2 lbs. 3 ozs. 48 drams

1 inch = 25.4 millimeters

1 pound avd. = 453.5925 grams 1 ounce avd. = 28.3495 grams1 grain = 0.0648 gram

English cubic inches.

1 U.S. gallon = 3.78543 liters 1 Imperial gallon = 4.54346 liters

1 U.S. quart = 0.94636 liter

1 fluidounce = 28.396 cubic centimeters

## Tables for Determination of Temperature.

#### RELATIONS BETWEEN THERMOMETERS.

In Fahrenheit's thermometer, the freezing-point of water is placed at 32°, and the boiling-point at 212°, and the number of intervening degrees is 180.

The Centigrade or Celsius's thermometer, which is now recognized in the U.S. Pharmacopæia and has been adopted generally by scientists, marks the freezing-point zero, and the boiling-point 100°.

From the above statement, it is evident that 180 degrees of Fahrenheit are equal to 100° of the Centigrade, or one degree of the first is equal to \( \frac{5}{6} \) of a degree of the second. It is easy, therefore, to convert the degrees of one into the equivalent number of degrees of the other; but in ascertaining the corresponding points upon the different scales, it is necessary to take into consideration their different modes of gradua-Thus, as the zero of Fahrenheit is 32° below the point at which that of the Centigrade is placed, this number must be taken into account in the calculation.

- 1. If any degree on the Centigrade scale, either above or below zero, be multiplied by 1.8, the result will, in either case, be the number of degrees above or below 32°, or the freezing-point of Fahrenheit.
- 2. The number of degrees between any point of Fahrenheit's scale and 32°, if divided by 1.8, will give the corresponding point on the Centigrade.

## APPENDIX.

## THERMOMETRIC EQUIVALENTS.

#### ACCORDING TO THE CENTIGRADE AND FAHRENHEIT SCALES.

						,			
g.º	æ.∘	C.º	F.º	0 °	F.º	C.º	F.º	C.º	F°.
-39.4	89	17.2	1	5	41	27.2	81	49.4	121
39	38.2	-17	1.4	5.5	42	27.7	82	50	122
-38.8	38	-16.6	2	6	42.8	28	82.4	50.5	123
38.3	-37	-16.1	3	6.1	43	28.3	83	51	123.8
- 38	36.4	16	3.2	6.6	44	28.8	84	51.1	124
-37.7	36	-15.5	4	7	44.6	29	84.2	51.6	125
-37.2	85	-15	5	7.2	45	29.4	85	52	125.6
37	34.6	-14.4	6	7.7	46 46.4	30 30.5	86 87	52.2 52.7	126
-36.6	-34 -33	14 13.8	6.8 7	8 8.3	40.4	30.5	87.8	53	127 127.4
-36.1 -36	-32.8	-13.8	8	8.8	48	31.1	88	53.3	128
35.5	-32.0 -32	-13	8.6	9.	48.2	31.6	89	53.8	129
35	-31	-12.7	9	9.4	49	82	89.6	54	129.2
-34.4	30	-12.2	10	10	50	32.2	90	54.4	130
34	-29.2	12	10.4	10.5	51	32.7	91	55	131
33.8	-29	11.6	11	11	51.8	33	91.4	55.5	132
-33.3	-28	11.1	12	11.1	52	33.3	92	56	132.8
-33	-27.4	-11	12.2	11.6	53	88.8	93	50.1	133
-32.7	-27	10.5	13	12	53.6	34 34.4	98.2	56.6	134
-32.2 -32	26 25.6	10 9.4	14 15	$12.2 \\ 12.7$	54 55	35	94 95	57 57.2	134.6 135
-31.6	-25.0 $-25$	—9.± —9	15.8	13.7	55.4	35.5	96	57.7	136
-31.1	-24	-8.8	16.0	13.3	56	86	96.8	58	186.4
31	23.8	-8.3	17	13.8	57	36.1	97	58.3	137
-30.5	-23	8	17.6	14	57.2	36.6	98	58.8	138
-30	22	<b>—7.7</b>	18	14.4	58	37	98.6	59	138.2
-29.4	21	-7.2	19	15	59	37.2	99	59.4	139
<b>—29</b>	-20.2	-7	19.4	15.5	60	37.7	100	60	140
-28.8	20	-6.6	20	16	60.8	38	100.4	60.5	141
-28.3 -28	—19 —18.4	6.1 6	$\begin{array}{c} 21 \\ 21.2 \end{array}$	16.1 16.6	61	38.3 38.8	101	61 61.1	141.8
-26 $-27.7$	—18. <del>*</del>	6 5.5	22	17	62.6	39	102.2	61.6	143
-27.2		_5.0	23	17.2	63	39.4	103	62	143.6
-27	-16.6	-4.4	24	17.7	64	40	104	62.2	144
-26.6	-16	-4	24.8	18	64.4	40.5	105	62.7	145
-26.1	<b>—15</b>	3.8	25	18.3	65	41	105.8	63	145.4
26	14.8	8.3	26	18.8	66	41.1	106	63.3	146
-25.5	<b>—14</b>	-8_	26.6	19	66.2	41.6	107	63.8	147
25	—18 —12	2.7 2.2	27	19.4	67	42 42.2	107.6	64	147.2
—24.4 —24	-12 -11.2		28 28.4	20 20.5	68 69	42.2	108 109	64.4 65	148 149
-23.8	—11.2 —11	_1.6	29	20.5	69.8	43	109.4	65.5	150
-23.3	_10	-1.1	30	21.1	70	43.3	110	66	150.8
-23	-9.4	_î	30.2	21.6	71	43.8	111	66.1	151
-22.7	—9	-0.5	31	22	71.6	44	111.2	66.6	152
-22.2	<u> </u>	0	82	22.2	72	44.4	112	67	152.6
-22	7.6	0.5	33	22.7	78	45	113	67.2	153
-21.6	<del>-7</del>	1 1	33.8	23	73.4	45.5	114	67.7	154
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	-6 -5.8	1.1	34	28.3	74	46	114.8	68	154.4
-21 -20.5	5.8 5	1.6	35 35.6	23.8 24	75 75.2	46.1 46.6	115	68.8	155
-20.5 -20		2.2	36.0 36	24.4	75.2	40.0	116.6	68.8 69	156 156.2
—20 —19.4		2.7	37	25	77	47.2	117	69.4	150.2
19	-2.2	3	37.4	25.5	78	47.7	118	70	158
-18.8	-2	3.3	38	26	78.8	48	118.4	70.5	159
18.3	1	8.8	89	26.1	79	48.8	119	71	159.8
—18	0.4	4.	39.2	26.6	80	48.8	120	71.1	160
<b>—17.7</b>	0	4.4	40	27	80.6	49	120.2	71.6	161
Į.	ا ا	1 '	•	1	!	I .	١ ١	I .	

APPENDIX.

## Thermometric Equivalents.—Continued.

C.º	F.º	G' <sub>0</sub>	F.º	C.º	F.º	G.º	F.º	C.º	F.º
72	161.6	95.5	204	118.8	246	142.2	288	166	330.8
72.2	162	96	204.8	119	246.2	142.7	289	166.1	331
72.7	163	96.1	205	119.4	247	143	289.4	166.6	332
73	163.4	96.6	206	120	248	143.3	290	167	332.6
73.3	164	97	206.6	120.5	249	143.8	291	167.2	383
73.8	165	97.2	207	121	249.8	144	291.2	167.7	384
74	165.2	97.7	208	121.1	250	144.4	292	168	384.4
74.4	166	98	208.4	121.6	251	145	293	168.3	885
75 75.5	167 168	98.3	209	122	251.6	145.5	294	168.8	836
76	168.8	98.8 99	210 210.2	122.2 122.7	252 253	146 146.1	294.8	169 169.4	336.2
76.1	169	99.4	210.2	123	258.4	146.6	295 296	170	337 338
76.6	170	100	212	123.3	254	147	296.6	170.5	339
77	170.6	100.5	213	123.8	255	147.2	297	171	339.8
77.2	171	101	213.8	124	255.2	147.7	298	171.1	340
77.7	172	101.1	214	124.4	256	148	298.4	171.6	341
78	172.4	101.6	215	125	257	148.3	299	172	341.6
78.8	173	102	215.6	125.5	258	148.8	300	172.2	842
78.8	174	102.2	216	126	258.8	149	300.2	172.7	343
79	174.2	102.7	217	126.1	259	149.4	301	173	343.4
79.4	175	103	217.4	126.6	260	150	802	173.8	344
80 80.5	176 177	103.3 103.8	218 219	127	260.6	150.5	303	173.8	345
81	177.8	103.8	219	127.2 127.7	261 262	151 151.1	303.8	174	345.2
81.1	178	104.4	220	128	262.4	151.6	304 305	174.4 175	346 347
81.6	179	105	221	128.8	263	151.0	305.6	175.5	348
82	179.6	105.5	222	128.8	264	152.2	306	176	348.8
82.2	180	106	222.8	129	264.2	152.7	307	176.1	349
82.7	181	106.1	223	129.4	265	153	307.4	176.6	350
83	181.4	106.6	224	180	266	158.3	308	177	350.6
83.3	182	107	224.6	180.5	267	153.8	309	177.2	351
88.8	183	107.2	225	131	267.8	154	309.2	177.7	352
84	183.2	107.7	226	131.1	268	154.4	810	178	852.4
84.4	184 185	108 108.3	226.4	131.6	269	155	311	178.3	358
85 85.5	186	108.8	227 228	132 132.2	269.6 270	155.5 156	312 312.8	178.8 179	854
86	186.8	109	228.2	132.7	271	156.1	313	179.4	854.2 855
86.1	187	109.4	229	133	271.4	156.6	314	180	356
86.6	188	110	230	133.3	272	157	314.6	180.5	357
87	188.6	110.5	231	133.8	273	157.2	815	181	357.8
87.2	189	111	231.8	134	273.2	157.7	316	181.1	358
87.7	190	111.1	232	134.4	274	158	816.4	181.6	359
88	190.4	111.6	288	135	275	158.3	317	182	859.6
88.3	191	112 112.2	283.6	135.5	276	158.8	318	182.2	860
88.8	192		234	136	276.8	159	818.2	182.7	361
89	192.2	112.7	235 235.4	136.1 136.6	277 278	159.4	819	183	361.4
89.4 90	193 194	113 113.8	236	137	278.6	160 160.5	820 821	183.3 183.8	362 363
90.5	195	113.8	287	137.2	279	161	321.8	184	863. <b>2</b>
91	195.8	114	237.2	137.7	280	161.1	322	184.4	364
91.1	196	114.4	238	138	280.4	161.6	323	185	365
91.6	197	115	289	138.3	281	162	323.6	185.5	866
92	197.6	115.5	240	138.8	282	162.2	324	186	366.8
92.2	198	116	240.8	139	282.2	162.7	325	186.1	367
92.7	199	116.1	241	139.4	283	163	325.4	186.6	368
98	199.4	116.6	242	140	284	163.3	826	187	368.6
93.3	200	117	242.6	140.5	285	168.8	327	187.2	369
93.8	201	117.2	243	141	285.8	164	827.2	187.7	370 970 4
94.4	201.2 202	117.7 118	244 244.4	141.1 141.6	286 287	164.4	828 829	188 188.3	370.4
95	202	118.3	245	141.6	287.6	165 165.5		188.8	371 372
1 00	200	110.0	230	172	201.0	100.0	300	100.0	014

Thermometric Equivalents.—Continued.

APPENDIX.

	1	<del></del>	<del></del>	<u> </u>	1		1		
G.º	F.º	C.º	F.°	C.º	F.º	C.º	F.º	Q.º	F.º
189	372.2	211.6	413	283.8	458	256.1	493	278.3	533
189.4	378	212	413.6	234	453.2	256.6	494	278.8	584
190	374	212.2	414	234.4	454	257	494.6	279	534.2
190.5	875	212.7	415	235	455	257.2	495	279.4	535
191	375.8	213	415.4	235.5	456	257.7	496	280	536
191.1	376	213.3	416	286	456.8	258	496.4	280.5	537
191.6	877	213.8	417	236.1	457	258.3	497	281	537.8
192	377.6	214	417.2	236.6	458	258.8	498	281.1	538
192.2	378	214.4	418	287	458.6	259	498.2	281.6	539
192.7	379	215	419	237.2	459	259.4	499	282	539.6
198	879.4	215.5	420	237.7	460	260	500	282.2	540
193.3	380	216	420.8	238	460.4	260.5	501	282.7	541
193.8	381	216.1	421	238.3	461	261	501.8	283	541.4
194	381.2	216.6	422	238.8	462	261.1	502	283.3	542
194.4	382	217	422.6	239	462.2	261.6	508	283.8	548
195	883	217.2	423	239.4	468	262	503.6	284	543.2
195.5	384	217.7	424	240	464	262.2	504	284.4	544
196	384.8	218	424.4 425	240.5 241	465 465.8	262.7 263	505 505.4	285	545 546
196 1	885	218.3	425 426	241.1	466	263.3	506	285.5 286	546.8
196.6	386	218.8	426.2	241.1	467	263.8	507	286.1	547
197 197.2	386.6 387	219 219.4	427	241.0	467.6	264	507.2	286.6	548
197.7	388	219.4	428	242.2	468	264.4	508	287	548.6
197.7	388.4	220.5	429	242.7	469	265	509	287.2	549
198.3	389	220.5	429.8	243	469.4	265.5	510	287.7	550
198.8	890	221.1	480	243.3	470	266	510.8	288	550.4
199	390.2	221.6	431	243.8	471	266.1	511	288.3	551
199.4	391	222	481.6	244	47. 2	266.6	512	288.8	552
200	392	222.2	482	244 4	472	267	512.6	289	552.2
200.5	393	222.7	433	245	478	267.2	518	289.4	553
201	393.8	223	433.4	245.5	474	267.7	514	290	554
201.1	394	223.3	434	246	474.8	268	514.4	290.5	555
201.6	395	223.8	435	246.1	475	268.3	515	291	555.8
202	395.6	224	485.2	246.6	476	268.8	516	291.1	556
202.2	896	224.4	486	247	476.6	269	516.2	291.6	557
202.7	397	225	437	247.2	477	269.4	517	292	557.6
208	897.4	225.5	438	247.7	478 478.4	270 270.5	518 519	292.2 292.7	558 559
203.3 203.8	398 399	226 226.1	438.8 439	248 248.3	479	270.5	519.8	298	559.4
203.6	399.2	226.6	440	248.8	480	271.1	520	293.3	560
204.4	400	227	440.6	249	480.2	271.6	521	298.8	561
205	401	227.2	441	249.4	481	272	521.6	294	561.2
205.5	402	227.7	442	250	482	272.2	522	294.4	562
206.5	402.8	228	442.4	250.5	483	272.7	523	295	563
206.1	403	228 3	443	251	483.8	273	523.4	295.5	564
206.6	404	228.8	444	251.1	484	278.8	524	296	564.8
207	404.6	229	444.2	251.6	485	273.8	525	296.1	565
207.2	405	229.4	445	252	485.6	274	525.2	296.6	566
207.7	406	280	446	252.2	486	274.4	526	297	566.6
208	406.4	280.5	447	252.7	487	275	527	297.2	567
208.3	407	281	447.8	253	487.4	275.5	528	297.7	568
208.8	408	231.1	448	253.3	488	276	528.8	298	568.4
209	408.2	231.6	449	253.8	489	276.1	529	298.3	569
209.4	409	232	449.6	254	489.2	276.6	580	298.8	570
210	410	232.2	450	254.4	490	277	530.6	299 .	570.2
210.5	411	282.7	451	255	491	277.2	531	299.4	571
211	411.8	233	451.4	255.5	492	277.7	582	800	572
211.1	412	233.3	452	256	492.8	278	582.4		
L	1	11	1	11	1	1		· · · · · · · · · · · · · · · · · · ·	

## III. Specific Gravity Tables.

### 1. Baumé's Scale for Liquids Lighter than Water.

The following table is calculated for a temperature of 17.5° C. (63.5° F.), and is based on the formulas  $\frac{140}{\text{B.°} + 130}$  = specific gravity and  $\frac{140}{\text{specific gravity}}$  = 130 = B.°.

Degree Baumé.	Specific gravity.	Degree Baumé.	Specific gravity.	Degree Baumé.	Specific gravity.	Degree Baumé.	Specific gravity.
10	1.0000	88	0.8588	56	0.7526	79	0.6698
11	0.9929	34	0.8586	57	0.7486	80	0.6666
12	0.9859	35	0.8484	58	0.7446	81	0.6635
18	0.9790	86	0.8433	59	0.7407	82	0.660 <del>4</del>
14	0.9722	87	0.8383	60	0.7868	83	0.6578
15	0.9655	88	0.8333	61	0.7329	84	0.6542
16	0.9589	89	0.8284	62	0.7290	85	0.6511
17	0.9523	40	0.8285	68	0.7258	86	0.6482
18	0.9459	41 °	0.8187	64	0.7216	87	0.6452
19	0.9395	42	0.8139	65	0.7179	88	0.6422
20	0.9333	43	0.8092	66	0.7142	89 1	0.6393
21	0.9271	44	0.8045	67	0.7106	90	0.6368
22	0.9210	45	0.8000	68	0.7070	91	0.6885
28	0.9150	46	0.7954	l 69	0.7035	92	0 6806
24	0.9090	47	0.7909	70	0.7000	98	0.6278
25	0.9032	48	0.7865	71	0.6965	94	0.6250
26	0.8974	49	0.7821	72	0.6981	95	0.6222
27	0.8917	50	0.7777	78	0.6896	96	0.6195
28	0.8860	51	0.7734	74	0.6868	97	0.6167
29	0.8805	52	0.7692	75	0.6829	98	0.6140
80	0.8750	<b>5</b> 8	0.7650	76	0.6796	99	0.6118
31	0.8695	54	0.7608	77	0.6763	100	0.6087
82	0.8641	55	0.7567	78	0.6731		

The coefficient of expansion of petroleum oils for increase or decrease of 1° C. in temperature has been determined for both Russian and American oils. For the latter the following figures have been given (*Iron Age*, xxxviii, No. 7):

Specific gravity at 15° C. (59° F.).													е	Coefficient of cansion for 1° C.
Under 0.700 .														0.00090
0.700 to 0.750														0.00085
0.750 to 0.800														0.00080
0.800 to 0.815														0.00070
Over 0.815			_											0.00065

As stated in the text (p. 39), it is customary in practice to take as the coefficient of expansion 0.004 for every 10° F. (0.00072 for 1° C.).

2. Comparison of Various Baumé Hydrometers for Liquids Heavier than Water with Specific Gravities. (Lunge's Technical Methods of Chemical Analysis, vol. i, p. 935.)

1 54 /	Rational Hydrometer $d = \frac{144.3}{144.3 - n}$	Baumé's Hydrometer according to Gerlach's scale.	Baumé American scale $d = \frac{145}{145 - n}$	Degrees.	Rational Hydrometer $d = \frac{144.3}{144.3 - n}$	Baumé's Hydrometer according to Gerlach's scale.	Baumé American scale $d = \frac{145}{145 - n}$
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 24 25 26 27 28 29 30 31 32 33 33 33 33 33 33 33 33 33 33 33 33	1.007 1.014 1.022 1.029 1.037 1.045 1.052 1.060 1.067 1.075 1.083 1.100 1.108 1.116 1.125 1.134 1.142 1.152 1.162 1.171 1.180 1.190 1.200 1.210 1.220 1.231 1.241 1.252 1.263 1.274 1.285 1.297	1.0068 1.0188 1.0208 1.0280 1.0353 1.0426 1.0501 1.0576 1.0653 1.0731 1.0810 1.0890 1.0972 1.1054 1.1138 1.1224 1.1310 1.1398 1.1487 1.1578 1.1670 1.1763 1.1858 1.1955 1.2053 1.2153 1.2254 1.2357 1.2462 1.2369 1.2677 1.2788 1.2901	1.005 1.011 1.023 1.029 1.036 1.043 1.050 1.057 1.064 1.071 1.086 1.093 1.100 1.107 1.114 1.122 1.136 1.143 1.150 1.158 1.172 1.179 1.186 1.201 1.208 1.216 1.231 1.238 1.254 1.262 1.269 1.285 1.293	34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 66 61 62 63 64 65 66	1.808 1.320 1.332 1.345 1.357 1.370 1.383 1.397 1.410 1.424 1.438 1.453 1.468 1.483 1.498 1.514 1.530 1.540 1.568 1.580 1.597 1.615 1.634 1.652 1.671 1.691 1.771 1.792 1.753 1.774 1.796 1.819 1.842	1.3015 1.3181 1.3250 1.3870 1.3494 1.3619 1.3746 1.3876 1.4009 1.4134 1.4281 1.4421 1.4564 1.4710 1.4860 1.5012 1.5167 1.5325 1.5487 1.5652 1.5820 1.5993 1.6169 1.6349 1.6533 1.6721 1.6914 1.7111 1.7818 1.7520 1.7781 1.7948 1.8171	1.309 1.317 1.334 1.342 1.359 1.368 1.386 1.395 1.413 1.422 1.441 1.451 1.470 1.480 1.500 1.510 1.581 1.541 1.561 1.573 1.594 1.616 1.627 1.650 1.661 1.683 1.705 1.727 1.747 1.767 1.793 1.814 1.835

What is known as the "Rational" Baumé scale is calculated by taking water at the temperature chosen at 0° B. and sulphuric acid of 1.842 specific gravity at 66° B. and using the formula  $\frac{144.3}{144.3-n^{\circ}}=d.$  (See Lunge's "Sulphuric Acid and Alkali," vol. i., p. 20.)

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3.	Twaddle's	Scale	for	Liquids	Heavier	than	Water.
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Degrees Twaddle.	Specific gravity.	Degrees Twaddle.	Specific gravity.	Degrees Twaddle.	Specific gravity.	Degrees Twaddle.	Specific gravity.	Degrees Twaddle.	Specific gravity.	Degrees Twaddle.	Specific gravity.	Degrees Twaddle.	Specific gravity.
0 1 1 2 2 3 4 4 5 5 6 6 7 7 8 9 9 1 1 1 1 2 1 3 1 1 4 1 5 1 6 1 1 7 1 1 8 9 2 0 2 1 1 2 2 2 2 2 2 2 2 2 2 2 2 2 4 1 1 1 2 2 2 2	1.000 1.005 1.010 1.015 1.020 1.025 1.030 1.035 1.040 1.045 1.050 1.055 1.065 1.070 1.075 1.080 1.095 1.100 1.105 1.1100 1.115 1.110	29 30 31 32 38 38 36 37 38 39 40 41 42 43 44 45 46 47 48 50 51 52 53	1.145 1.150 1.155 1.165 1.165 1.170 1.175 1.180 1.195 1.200 1.215 1.210 1.225 1.225 1.220 1.225 1.235 1.240 1.255 1.260 1.266	58 59 60 61 62 68 64 65 66 67 71 72 78 79 80 81 82	1.290 1.295 1.300 1.315 1.310 1.315 1.320 1.320 1.345 1.340 1.345 1.355 1.360 1.365 1.370 1.385 1.380 1.385 1.380 1.385 1.380	87 · 88 89 90 91 92 93 94 95 96 97 98 99 100 101 102 103 104 105 106 107 108 109 110	1.485 1.440 1.445 1.455 1.460 1.465 1.470 1.475 1.480 1.485 1.505 1.505 1.510 1.515 1.520 1.520 1.525 1.540 1.540 1.555	116 117 118 119 120 121 122 123 124 125 126 127 128 129 180 181 182 183 184 185 186 187 188	1.580 1.585 1.590 1.695 1.605 1.610 1.615 1.625 1.630 1.635 1.640 1.655 1.650 1.655 1.660 1.675 1.670 1.675 1.680 1.685	145 146 147 148 149 150 151 152 153 154 155 156 157 158 160 161 162 168 164 165 166 167	1.725 1.780 1.785 1.745 1.745 1.750 1.755 1.760 1.775 1.770 1.775 1.780 1.795 1.800 1.805 1.815 1.820 1.825 1.830 1.825 1.830	178 174 175 176 177 178 180 181 182 188 184 185 186 187 190 191 192 192 194 195 196 197	1.865 1.870 1.875 1.885 1.890 1.895 1.900 1.915 1.910 1.915 1.920 1.920 1.945 1.940 1.945 1.955 1.960 1.965 1.970 1.980
25 26 27 28	1.125 1.130 1.185 1.140	54 55 56 57	1.270 1.275 1.280 1.285	83 84 85 86	1.415 1.420 1.425 1.480	112 113 114 115	1.560 1.565 1.570 1.575	141 142 143 144	1.705 1.710 1.715 1.720	170 171 172	1.850 1.855 1.860	198 199 200	1.990 1.995 2.000

The uniform division of the Twaddle scale makes the degrees very easily convertible into specific gravity readings. It is only necessary to multiply the degree as read off by five and add this to 1.000 in order to obtain the specific gravity.

Again, as the gallon of distilled water at ordinary temperatures weighs ten pounds avoirdupois, it is possible to determine the weight of a gallon of an acid or lye by the aid of the Twaddle scale. Thus, if an acid shows 50° Twaddle, corresponding to the specific gravity 1.250, it weighs twelve and a half pounds per gallon. Or, as a liter of distilled water weighs one thousand grams, a liter of a liquid showing 20° Twaddle will weigh eleven hundred grams.

## 4. Comparison of the Twaddle Scale with the Rational Baumé Scale.

5. Comparison between Specific Gravity Figures, Degree Baumé and Degree Brix (as used for sugar solutions).

Percentage of sugar ac- cording to Balling or degree Brix.	Specific gravity.	Degree Baumė.	Percentage of sugar ac- cording to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar ac- cording to Balling or degree Brix.	Specific gravity.	Degree Baumé.
0.0 0.1 0.2 0.8 0.4 0.5 0.6 0.7 0.8	1.00000 1.00038 1.00077 1.00116 1 00155 1.00193 1.00282 1.00271 1.00810 1.00849	0.00 0.06 0.11 0.17 0.28 0.28 0.34 0.40 0.45	5.0 5.1 5.2 5.3 5.4 5.5 5.6 5.7 5.8 5.9	1.01970 1.02010 1.02051 1.02091 1.02181 1.02171 1.02211 1.02252 1.02292 1.02388	2.84 2.89 2.95 3.01 3.06 3.12 3.18 3.29 3.35	10.0 10.1 10.2 10.3 10.4 10.5 10.6 10.7 10.8 10.9	1.04014 1.04055 1.04097 1.04139 1.04180 1.04222 1.04264 1.04306 1.04848 1.04890	5.67 5.72 5.78 5.83 5.89 5.95 6.00 6.06 6.12 6.17
1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8	1.00888 1.00427 1.00466 1.00505 1.00544 1.00588 1.00622 1.00662 1.00701 1.00740	0.57 0.68 0.68 0.74 0.80 0.85 0.91 0.97 1.02 1.08	6.0 6.1 6.2 6.8 6.4 6.5 6.6 6.7 6.8 6.9	1.02378 1.02413 1.02454 1.02494 1.02585 1.02575 1.02616 1.02657 1.02697 1.02738	3.40 3.46 3.52 3.57 3.63 3.69 3.74 3.80 3.86 3.91	11.0 11.1 11.2 11.8 11.4 11.5 11.6 11.7 11.8 11.9	1.04431 1.04478 1.04515 1.04557 1.04599 1.04641 1.04688 1.04726 1.04768 1.04810	6.28 6.29 6.34 6.40 6.46 6.51 6.57 6.62 6.68
2.0 2.1 2.2 2.8 2.4 2.5 2.6 2.7 2.8 2.9	1.00779 1.00818 1.00858 1.00859 1.00996 1.00976 1.01015 1.01055 1.01094 1.01134	1.14 1.19 1.25 1.31 1.36 1.42 1.48 1.53 1.59 1.65	7.0 7.1 7.2 7.8 7.4 7.5 7.6 7.7 7.8 7.9	1.02779 1.02819 1.02860 1.02901 1.02942 1.02983 1.08024 1.08064 1.08105 1.08148	8.97 4.08 4.08 4.14 4.20 4.25 4.31 4.87 4.42 4.48	12.0 12.1 12.2 12.3 12.4 12.5 12.6 12.7 12.8 12.9	1.04852 1.04894 1.04987 1.04979 1.05021 1.05064 1.05106 1.05149 1.05288	6.79 6.85 6.91 6.96 7.02 7.08 7.18 7.19 7.24 7.30
8.0 8.1 8.2 8.3 8.4 8.5 8.6 8.7 8.8 8.9	1.01178 1.01213 1.01252 1.01292 1.01292 1.01371 1.01411 1.01451 1.01491 1,01581	1.70 1.76 1.82 1.87 1.93 1.99 2.04 2.10 2.16 2.21	8.0 8.1 8.2 8.3 8.4 8.5 8.6 8.7 8.8 8.9	1.08187 1.08228 1.08270 1.08311 1.08352 1.03398 1.03484 1.03475 1.03558	4.58 4.59 4.65 4.70 4.76 4.82 4.87 4.98 4.99 5.04	18.0 13.1 18.2 18.3 18.4 18.5 18.6 18.7 18.8 13.9	1.05276 1.05318 1.05361 1.05404 1.05446 1.05489 1.05582 1.05574 1.05660	7.86 7.41 7.47 7.53 7.58 7.64 7.69 7.75 7.81
4.0 4.1 4.2 4.3 4.4 4.5 4.6 4.7 4.8 4.9	1.01570 1.01610 1.01650 1.01690 1.01730 1.01770 1.01810 1.01850 1.01890 1.01930	2.27 2.33 2.38 2.44 2.50 2.55 2.61 2.67 2.72 2.78	9.0 9.1 9.2 9.3 9.4 9.5 9.6 9.7 9.8 9.9	1.08599 1.08640 1.08682 1.08765 1.03806 1.03848 1.03889 1.08931 1.08972	5.10 5.16 5.21 5.27 5.33 5.38 5.44 5.50 5.55 5 61	14.0 14.1 14.2 14.8 14.4 14.5 14.6 14.7 14.8 14.9	1 05703 1.05746 1.05789 1.05831 1.05874 1.05917 1.05960 1.06003 1.06047 1.06090	7.92 7.98 8.03 8.09 8.14 8.20 8.26 8.31 8.37 8.43

APPENDIX.

# Comparison between Specific Gravity Figures, Degree Baumé and Degree Brix.—Continued.

Percentage of sugar ac- cording to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar ac- cording to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar ac- cording to Balling or degree Brix.	Specific gravity.	Degree Baumé.
15.0 15.1 15.2 15.8 16.4 15.5 15.6 15.7 15.8 15.9	1.06133 1.06176 1.06219 1.06262 1.06806 1.06849 1.06892 1.06479 1.06522	8.48 8.54 8.59 8.65 8.71 8.76 8.82 8.88 8.93 8.99	20.0 20.1 20.2 20.8 20.4 20.5 20.6 20.7 20.8 20.9	1.08329 1.08374 1.08419 1.08464 1.08509 1.08558 1.08599 1.08648 1.08688 1.08738	11.29 11.34 11.40 11.45 11.51 11.57 11.62 11.68 11.78 11.79	25.0 25.1 25.2 25.8 25.4 25.6 25.6 25.7 25.8 25.9	1.10607 1.10658 1.10700 1.10746 1.10798 1.10889 1.10886 1.10982 1.10979 1.11026	14.08 14.18 14.19 14.24 14.80 14.85 14.41 14.47 14.52 14.58
16.0 16.1 16.2 16.3 16.4 16.5 16.6 16.7 16.8 16.9	1.06566 1.06609 1.06653 1.06696 1.06740 1.06788 1.06827 1.06827 1.06914 1.06958	9.04 9.10 9.16 9.21 9.27 9.38 9.44 9.49 9.55	21.0 21.1 21.2 21.3 21.4 21.5 21.6 21.7 21.8 21.9	1.08778 1.08824 1.08869 1.08914 1.08959 1.09049 1.09095 1.09140 1.09185	11.85 11.90 11.96 12.01 12.07 12.18 12.18 12.24 12.29 12.85	26.0 26.1 26.2 26.8 26.4 26.5 26.6 26.7 26.8 26.9	1.11072 1.11119 1.11166 1.11218 1.11259 1.11306 1.11358 1.11400 1.11447 1.11494	14.68 14.69 14.74 14.80 14.85 14.91 14.97 15.02 15.08 15.18
17.0 17.1 17.2 17.3 17.4 17.5 17.6 17.7 17.8 17.9	1.07002 1.07046 1.07090 1.07138 1.07177 1.07221 1 07265 1.07309 1.07358 1.07397	9.61 9.66 9.72 9.77 9.88 9.89 9.94 10.00 10.06 10.11	22.0 22.1 22.2 22.3 22.4 22.5 22.6 22.7 22.8 22.9	1.09281 1.09276 1.09321 1.09867 1.09412 1.09458 1.09503 1.09549 1.09595 1.09640	12.40 12.46 12.52 12.57 12.68 12.68 12.74 12.80 12.85 12.91	27.0 27.1 27.2 27.8 27.4 27.5 27.6 27.7 27.8 27.9	1.11541 1.11588 1.11685 1.11682 1.11729 1.11776 1.11824 1.11871 1.11918 1.11965	15.19 15.24 15.80 15.85 15.41 15.46 15.52 15.58 15.68 15.69
18.0 18.1 18.2 18.3 18.4 18.5 18.6 18.7 18.8 18.9	1.07441 1.07485 1.07530 1.07574 1.07618 1 07662 1.07706 1.07751 1.07795	10.17 10.22 10.28 10.38 10.39 10.45 10.50 10.56 10.62	28.0 28.1 28.2 28.3 28.4 28.5 28.6 28.6 28.7 28.8 28.9	1.09686 1.09782 1.09777 1.09828 1.09869 1.09915 1.09061 1.10007 1.10058 1.10099	12.96 18.02 18.07 18.13 18.19 18.24 18.30 18.35 18.41 18.46	28.0 28.1 28.2 28.3 28.4 28.5 28.6 28.7 28.8 28.9	1.12018 1.12060 1.12107 1.12155 1.12202 1.12250 1.12297 1.12345 1.12398 1.12440	15.74 15.80 15.85 15.91 15.96 16.02 16.07 16.18 16.18
19.0 19.1 19.2 19.3 19.4 19.5 19.6 19.7 19.8 19.9	1.07884 1.07928 1.07973 1.08017 1.08062 1.08106 1.08151 1 08196 1.08240 1.08285	10.78 10.78 10.84 10.90 10.95 11.01 11.06 11.12 11.18 11.27	24.0 24.1 24.2 24.3 24.4 24.5 24.6 24.7 24.8 24.9	1.10145 1.10191 1.10287 1.10283 1.10329 1.10875 1.10421 1.10468 1.10514 1.10560	13.52 18.58 18.63 18.69 18.74 18.80 18.85 18.91 18.96 14.02	29.0 29.1 29.2 29.3 29.4 29.5 29.6 29.7 29.8 29.9	1.12488 1.12536 1.12583 1.12631 1.12679 1.12727 1.12775 1.12828 1.12871 1.12919	16.80 16.85 16.41 16.46 16.52 16.67 16.68 16.74 16.79

Comparison between Specific Gravity Figures, Degree Baumé and Degree Brix.—Continued.

Percentage of sugar ac- cording to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar ac- cording to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar ac- cording to Balling or degree Brix.	Specific gravity.	Degree Baumé.
80.0 80.1 30.2 30.3 30.4 80.5 80.6 30.7 80.8 30.9	1.12967 1.18015 1.18068 1.18111 1.18159 1.18207 1.13255 1.18304 1.18352 1.18400	16.85 16.90 16.96 17.01 17.07 17.12 17.18 17.28 17.29 17.85	85.0 85.1 85.2 85.8 85.4 85.5 85.6 85.7 85.8	1.15411 1.15461 1.15511 1.15561 1.15611 1.15661 1.15710 1.15760 1.15810 1.15861	19.60 19.66 19.71 19.76 19.82 19.87 19.98 20.04 20.09	40.0 40.1 40.2 40.3 40.4 40.5 40.6 40.7 40.8 40.9	1,17948 1,17995 1,18046 1,18098 1,18150 1,18201 1,18253 1,18305 1,18357 1,18408	22.38 22.38 22.44 22.49 22.55 22.60 22.66 22.71 22.77 22.82
81.0	1.13449	17.40	86.0	1.15911	20.15	41.0	1.18460	22.87
81.1	1.13497	17.46	86.1	1.15961	20.20	41.1	1.18512	22.93
81.2	1.13545	17.51	86.2	1.16011	20.26	41.2	1.18564	22.98
81.3	1.13594	17.57	86.3	1.16061	20.31	41.3	1.18616	23.04
81.4	1.13692	17.62	86.4	1.16111	20.37	41.4	1.18688	28.09
81.5	1.13691	17.68	86.5	1.16112	20.42	41.5	1.18720	28.15
81.6	1.13740	17.78	86.6	1.16212	20.48	41.6	1.18772	23.20
81.7	1.13788	17.79	86.7	1.16202	20.53	41.7	1.18824	23.25
81.8	1.13837	17.84	86.8	1.16313	20.59	41.8	1.18887	23.31
81.9	1.13885	17.90	36.9	1.16363	20.64	41.9	1.18929	28.36
82.0	1.18984	17.95	87.0	1.16413	20.70	42.0	1.18981	28.42
82.1	1.18983	18.01	87.1	1.16464	20.75	42.1	1.19033	28.47
82.2	1.14032	18.06	87.2	1.16564	20.80	42.2	1.19086	28.52
82.3	1.14081	18.12	87.8	1.16565	20.86	42.3	1.19138	28.58
82.4	1.14129	18.17	87.4	1.16616	20.91	42.4	1.19190	23.68
82.5	1.14178	18.23	87.5	1.16666	20.97	42.5	1.19243	28.69
82.6	1.14227	18.28	87.6	1.16717	21.02	42.6	1.19295	28.74
82.7	1.14276	18.34	87.7	1.16768	21.08	42.7	1.19348	28.79
82.8	1.14825	18.39	87.8	1.16818	21.18	42.8	1.19400	28.85
82.9	1.14374	18.45	87.9	1.16869	21.19	42.9	1.19453	28.90
88.0	1.14428	18.50	38.0	1.16920	21.24	48.0	1.19505	23.96
88.1	1.14472	18.56	38.1	1.16971	21.30	43.1	1.19558	24.01
88.2	1.14521	18.61	38.2	1.17022	21.35	43.2	1.19611	24.07
88.3	1.14570	18.67	38.3	1.17072	21.40	48.3	1.19663	24.12
83.4	1.14620	18.72	38.4	1.17122	21.46	43.4	1.19716	24.17
88.5	1.14669	18.78	38.5	1.17174	21.51	43.5	1.19769	24.28
88.6	1.14718	18.83	38.6	1.17225	21.57	43.6	1.19822	24.28
88.7	1.14767	18.89	38.7	1.17276	21.62	43.7	1.19875	24.34
83.8	1.14817	18.94	38.8	1.17827	21.68	43.8	1.19927	24.39
83.9	1.14866	19.00	38.9	1.17879	21.78	43.9	1.19980	24.44
34.0	1.14915	19.05	39.0	1.17480	21.79	44.0	1.20033	24.50
34.1	1.14965	19.11	39.1	1.17481	21.84	44.1	1.20086	24.55
34.2	1.15014	19.16	39.2	1.17582	21.90	44.2	1.20139	24.61
34.3	1.15064	19.22	39.3	1.17583	21.95	44.3	1.20192	24.66
84.4	1.15118	19.27	39.4	1.17685	22.00	44.4	1.20245	24.71
84.5	1.15128	19.38	39.5	1.17686	22.06	44.5	1.20299	24.77
34.6	1.15218	19.38	39.6	1.17787	22.11	44.6	1.20352	24.82
84.7	1.15262	19.44	39.7	1.17789	22.17	44.7	1.20405	24.88
34.8	1.15312	19.49	39.8	1.17840	22.22	44.8	1.20458	24.98
84.9	1.15302	19.55	89.9	1.17892	22.28	44.9	1.20512	24.98

APPENDIX.

Comparison between Specific Gravity Figures, Degree Baumé and Degree Brix.—Continued.

			Drix,—	-Contin	ucu.			
Percentage of sugar ac- cording to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar ac- cording to Balling or degree Brix.	Specific gravity.	Degree Baumé,	Percentage of sugar ac- cording to Balling or degree Brix,	Specific gravity.	Degree Baumé.
45.0 45.1 45.2 45.8 45.4 45.5 45.6 45.7 45.8 45.9	1.20565 1.20618 1.20672 1.20725 1.20779 1.20882 1.20886 1.20939 1.20993 1.21046	25.04 25.09 25.14 25.20 25.25 25.81 25.86 25.41 25.47 25.52	50.0 50.1 50.2 50.8 50.4 50.5 50.6 50.7 50.8 50.9	1.23278 1.23334 1.23389 1.23444 1.23499 1.23555 1.23610 1.23666 1.23721 1.23777	27.72 27.77 27.82 27.88 27.98 28.04 28.09 28.14 28.20	55.0 55.1 55.2 55.8 55.4 55.5 55.6 55.7 55.8 55.9	1.26086 1.26148 1.26200 1.26257 1.26814 1.26872 1.26429 1.26486 1.26544 1.26601	30.87 80.42 80.47 30.58 30.68 30.68 30.68 30.74 30.79 30.84
46.0 46.1 46.2 46.8 46.4 46.5 46.6 46.7 46.8 46.9	1.21100 1.21154 1.21208 1.21261 1.21315 1.21869 1.21428 1.21477 1.21581 1.21585	25.57 25.68 25.68 25.74 25.79 25.84 25.90 25.95 26.00	51.0 51.1 51.2 51.3 51.4 51.5 51.6 51.7 51.8 51.9	1.28882 1.28888 1.28948 1.28999 1.24055 1.24111 1.24166 1.24222 1.24278 1.24884	28.25 28.30 28.36 28.41 28.46 28.51 28.57 28.62 28.67 28.78	56.0 56.1 56.2 56.8 56.4 56.5 56.6 56.7 56.8 56.9	1.26658 1.26716 1.26778 1.26831 1.26889 1.26946 1.27004 1.27120 1.27177	80.89 80.95 81.00 81.05 81.10 81.16 81.21 81.26 81.81 81.87
47.0 47.1 47.2 47.8 47.4 47.5 47.6 47.7 47.8 47.9	1.21689 1.21698 1.21747 1.21802 1.21856 1.21910 1.21964 1.22019 1.22078 1.22127	26.11 26.17 26.22 26.27 26.83 26.88 26.48 26.49 26.54 26.59	52.0 52.1 52.2 52.3 52.4 52.5 52.6 52.7 52.8 52.9	1.24390 1.24446 1.24502 1.24558 1.24614 1.24670 1.24726 1.24782 1.24839 1.24895	28.78 28.83 28.89 28.94 28.99 29.05 29.10 29.15 29.20 29.26	57.0 57.1 57.2 57.8 57.4 57.6 57.6 57.7 57.8	1.27285 1.27298 1.27395 1.27409 1.27467 1.27525 1.27583 1.27641 1.27699 1.27758	31.42 31.47 81.52 31.58 81.68 81.78 81.79 81.84 81.89
48.0 48.1 48.2 48.3 48.4 48.5 48.6 48.7 48.8	1.22182 1.22286 1.22291 1.22345 1.22400 1.22455 1.22509 1.22564 1.22619 1.22673	26.65 26.70 26.75 26.81 26.86 26.92 26.97 27.02 27.08 27.18	53.0 53.1 53.2 53.3 53.4 53.5 53.6 53.7 53.8 53.9	1.24951 1.25008 1.25064 1.25120 1.25177 1.25238 1.25290 1.25847 1.25408 1.25460	29.81 29.36 29.42 29.47 29.52 29.57 29.63 29.68 29.78	58.0 58.1 58.2 58.8 58.4 58.5 58.6 58.7 58.8 58.9	1.27816 1.27874 1.27982 1.27991 1.28049 1.28107 1.28166 1.28224 1.28283 1.28342	81.94 82.00 82.05 82.10 82.15 82.20 82.26 82.31 82.86 82.41
49.0 49.1 49.2 49.8 49.4 49.5 49.6 49.7 49.8 49.9	1.22728 1.22788 1.22838 1.22898 1.22948 1.23008 1.23058 1.28113 1.23168 1.28223	27.18 27.24 27.29 27.34 27.40 27.45 27.50 27.50 27.61 27.66	54.0 54.1 54.2 54.3 54.4 54.5 54.6 54.7 54.8 54.9	1.25517 1.25573 1.25630 1.25687 1.25744 1.25801 1.25857 1.25914 1.25971 1.26028	29.84 29.89 29.94 30.00 30.05 30.10 30.16 30.21 30.26 30.31	59.0 59.1 59.2 59.3 59.4 59.5 59.6 59.7 59.8 59.9	1.28400 1.28459 1.28518 1.28576 1.28635 1.28694 1.28758 1.28812 1.28871 1.28930	82.42 82.52 82.57 82.62 82.67 32.73 32.78 82.88 82.88 82.98

Comparison between Specific Gravity Figures, Degree Baumé and Degree Brix.—Continued.

Company	Percentage of sugar ac- cording to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar ac- cording to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar ac- cording to Balling or degree Brix.	Specific gravity.	Degree Baumé.
60.1	<u> </u>	1 22020		]	1 21020			1 95099	
60.8         1.29166         88.14         65.8         1.32172         85.78         70.3         1.35277         88.28           60.5         1.29284         38.20         65.5         1.32294         35.88         70.6         1.35403         38.38           60.6         1.29488         38.30         65.6         1.32478         35.88         70.6         1.35403         38.48           60.7         1.32417         35.98         70.7         1.35503         38.48           60.9         1.29621         38.46         65.9         1.32539         36.04         70.9         1.85653         38.58           61.0         1.29561         38.51         66.0         1.32601         36.09         71.0         1.85720         38.63           61.1         1.29664         38.56         66.1         1.32601         36.09         71.0         1.85720         38.63           61.2         1.29790         38.61         66.2         1.32724         36.14         71.1         1.35847         38.73           61.4         1.29819         38.77         66.5         1.32908         36.24         71.3         1.35910         38.83           61.5         1.28918 <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>38.18</td>									38.18
60.4         1.29225 88.20         65.4         1.32294 85.88         70.4         1.35340 88.83         60.6         1.29343 83.25         65.5         1.32943 85.88         70.6         1.35466 38.43         60.7         1.29403 83.40         65.6         1.23455 35.88         70.7         1.35530 38.48         60.8         1.29421 85.98         70.7         1.35530 38.48         60.8         1.29478 35.98         70.7         1.35530 38.53         88.58         80.9         70.9         1.35530 38.53         88.58         80.9         70.9         1.35530 38.53         88.58         80.9         70.9         1.35535 38.58         80.9         70.9         1.35536 38.58         80.9         70.9         1.35536 38.58         80.9         70.9         1.35536 38.58         80.9         70.9         1.35536 38.58         80.9         70.9         1.35536 38.58         80.9         70.9         1.35536 38.58         80.9         70.9         1.35536 38.58         80.9         70.9         1.35575 38.58         80.9         70.9         1.35575 38.58         80.9         70.9         1.35575 38.58         80.9         70.9         1.35575 38.58         80.9         71.0         1.35576 38.58         80.9         71.0         1.355847 38.58         80.9         71.0         1.355847 38.58									
60.5         1.29284         88.25         65.5         1.32294         85.88         70.5         1.35403         88.48           60.6         1.29402         38.40         65.6         1.32355         35.88         70.6         1.35403         88.48           60.7         1.29401         38.40         65.8         1.32478         35.98         70.7         1.35530         38.48           60.9         1.29521         38.46         65.9         1.32539         36.04         70.9         1.35563         38.58           61.0         1.29561         38.51         66.0         1.32601         36.09         71.0         1.85720         38.63           61.1         1.29700         38.61         66.2         1.32724         36.19         71.2         1.35847         38.73           61.4         1.29799         38.66         66.3         1.32785         36.24         71.2         1.35847         38.73           61.5         1.29987         38.77         66.5         1.32908         36.34         71.5         1.35931         38.73           61.6         1.29988         38.87         66.6         1.32970         36.39         71.6         1.36047         38.9									
60.6         1.29448         83.80         65.6         1.32417         85.98         70.6         1.35460         38.46           60.8         1.29462         33.40         65.7         1.82417         35.98         70.8         1.35503         38.53           60.9         1.29521         38.46         65.9         1.32639         36.04         70.9         1.35056         38.53           61.0         1.29581         38.51         66.0         1.32601         36.09         71.0         1.35723         38.63           61.1         1.29646         38.56         66.1         1.32724         36.19         71.2         1.35847         38.73           61.4         1.29759         38.66         66.3         1.32724         36.19         71.2         1.35847         38.73           61.5         1.29988         38.82         66.6         1.32970         36.39         71.6         1.35071         38.88           61.6         1.29988         38.82         66.7         1.33081         36.45         71.7         1.36364         38.98           61.8         1.30057         38.99         66.8         1.33098         36.50         71.8         1.36488         39.0									
60.8         1.29462         38.46         65.9         1.82639         36.04         70.9         1.85656         38.53           61.0         1.29581         38.51         66.9         1.82639         36.04         71.0         1.85656         38.58           61.1         1.29646         38.56         66.1         1.82762         36.14         71.1         1.35783         38.63           61.2         1.29709         38.61         66.2         1.32724         36.19         71.2         1.35847         38.73           61.4         1.29819         33.71         66.4         1.82847         36.29         71.4         1.85974         38.86           61.6         1.29988         38.82         66.6         1.32970         36.39         71.5         1.86037         38.88           61.6         1.29988         38.87         66.7         1.33081         36.45         71.7         1.36134         38.98           61.8         1.30057         38.92         66.8         1.33098         36.50         71.8         1.36228         39.08           62.0         1.80177         34.08         67.1         1.38278         36.60         72.0         1.36355         39.1	60.6	1.29348	83.80	65.6	1.82355	35.88	70.6	1.35466	38.43
60.9         1.29621         88.46         66.9         1.82639         36.04         70.9         1.85656         38.58           61.0         1.29581         33.51         66.0         1.32601         36.09         71.0         1.85720         38.68           61.1         1.29646         38.56         66.1         1.82762         36.14         71.1         1.35783         38.68           61.8         1.29790         38.61         66.2         1.32784         36.24         71.3         1.35914         38.73           61.4         1.29819         33.71         66.4         1.32947         36.29         71.4         1.35974         38.83           61.6         1.29988         38.87         66.6         1.32970         36.39         71.6         1.36131         38.93           61.7         1.29998         38.87         66.7         1.38031         36.50         71.8         1.36228         39.08           61.8         1.30057         34.08         67.0         1.38217         36.60         72.0         1.36356         39.13           62.0         1.80177         34.08         67.0         1.38237         36.60         72.1         1.36494         39.9									
61.1         1.29646         83.66         66.1         1.32762         36.18         71.2         1.35847         38.73           61.8         1.29759         38.61         66.2         1.32724         36.19         71.2         1.35847         38.73           61.4         1.29819         38.71         66.4         1.324847         36.29         71.4         1.35910         38.78           61.5         1.29988         38.82         66.6         1.32907         36.39         71.6         1.36101         38.93           61.7         1.29998         38.87         66.7         1.38031         38.45         71.7         1.36164         38.93           61.8         1.30057         38.99         66.8         1.38093         36.50         71.8         1.36228         39.03           61.9         1.80117         34.08         67.0         1.38217         36.65         71.9         1.36222         39.08           62.0         1.80237         34.08         67.1         1.38278         36.65         72.1         1.36449         39.19           62.2         1.80297         34.13         67.2         1.38340         36.75         72.1         1.36449         39.									
61.2         1.29700         38.61         66.2         1.32724         36.19         71.2         1.35910         38.78           61.4         1.29819         38.77         66.4         1.32908         36.24         71.3         1.35910         38.78           61.6         1.29878         38.77         66.5         1.32908         36.34         71.5         1.36037         38.88           61.6         1.29988         38.82         66.6         1.82970         36.39         71.6         1.36011         38.98           61.8         1.30057         33.92         66.8         1.3393         36.50         71.8         1.36228         39.08           62.0         1.80177         34.03         67.0         1.38217         36.60         72.0         1.86355         39.13           62.1         1.30237         34.18         67.2         1.38340         36.70         72.2         1.86488         39.19           62.2         1.30476         34.28         67.5         1.38340         36.75         72.3         1.864919         39.19           62.2         1.30476         34.28         67.4         1.33440         36.75         72.3         1.86773         39.2									
61.8         1.29619         38.66         66.8         1.32785         36.24         71.8         1.35910         38.78           61.6         1.29878         38.77         66.5         1.32908         36.34         71.4         1.35974         38.88           61.6         1.29988         38.82         66.6         1.32970         36.89         71.6         1.36101         38.98           61.8         1.30057         38.92         66.8         1.38930         36.50         71.7         1.36164         38.98           61.9         1.30117         34.03         66.9         1.38155         36.55         71.9         1.36292         39.08           62.0         1.30177         34.08         67.0         1.38217         36.60         72.0         1.86355         39.13           62.1         1.30287         34.08         67.1         1.38340         36.70         72.2         1.86483         39.24           62.2         1.30466         34.18         67.2         1.38340         36.75         72.2         1.86483         39.24           62.5         1.80476         34.28         67.4         1.33484         36.85         72.5         1.86673         39.3									
61.4									
61.6         1.29988         83.82         66.6         1.32970         36.89         71.6         1.36101         38.93           61.7         1.29998         33.87         66.7         1.33031         36.45         71.7         1.36164         38.98           61.9         1.30117         33.92         66.8         1.38098         36.55         71.9         1.36292         39.08           62.0         1.30177         34.03         67.0         1.38217         36.60         72.0         1.36292         39.08           62.1         1.30287         34.03         67.1         1.38278         36.65         72.1         1.36491         39.19           62.2         1.30297         34.13         67.2         1.38340         36.70         72.2         1.36483         39.29           62.3         1.30466         34.23         67.4         1.33464         36.80         72.4         1.36483         39.29           62.4         1.30476         34.23         67.5         1.38526         36.85         72.5         1.36675         39.39           62.6         1.30586         34.39         67.7         1.38526         36.96         72.7         1.36803         39.4					1.32847	36.29	71.4	1.35974	38.83
61.7         1.29998         83.87         66.7         1.38081         36.45         71.7         1.36164         38.98           61.9         1.30117         33.92         66.8         1.33093         36.50         71.9         1.36292         39.08           62.0         1.30177         34.08         67.0         1.38217         36.60         72.0         1.36855         39.13           62.1         1.30237         34.08         67.1         1.38218         36.67         72.1         1.36419         39.19           62.2         1.30297         34.18         67.2         1.38402         36.70         72.2         1.364319         39.19           62.2         1.30356         34.18         67.3         1.38402         36.75         72.3         1.36647         39.29           62.4         1.30416         34.23         67.4         1.33404         36.80         72.4         1.36611         39.39           62.6         1.30536         34.34         67.6         1.33588         36.90         72.6         1.36739         39.44           62.7         1.30596         34.39         67.7         1.38650         36.96         72.7         1.36803         39.									
61.8         1.80067         33.92         66.8         1.83153         36.55         71.9         1.86292         39.08           62.0         1.80177         34.08         67.0         1.83217         36.60         72.0         1.36355         39.13           62.1         1.80287         34.08         67.1         1.83278         36.65         72.1         1.36419         39.19           62.2         1.80297         34.13         67.2         1.8340         36.70         72.2         1.86483         39.24           62.2         1.80366         34.18         67.3         1.83402         36.70         72.2         1.86483         39.24           62.4         1.80416         34.23         67.4         1.83464         36.80         72.4         1.86671         39.39           62.6         1.80547         34.28         67.5         1.83526         36.85         72.5         1.86675         39.39           62.2         1.80596         34.39         67.7         1.83630         36.96         72.7         1.36893         39.44           62.9         1.30717         34.49         67.9         1.33774         37.01         72.8         1.36867         39.54									
62.0	61.8	1.30057	88.92	66.8	1.33093	36.50	71.8	1.36228	89.08
62.1         1.80287         34.08         67.1         1.83278         36.65         72.1         1.86419         39.19           62.2         1.80297         34.18         67.2         1.83840         36.70         72.2         1.86489         39.29           62.3         1.80416         34.28         67.4         1.83464         36.80         72.4         1.86611         39.39           62.5         1.80476         34.28         67.5         1.83526         36.85         72.5         1.86675         39.39           62.6         1.30536         34.34         67.6         1.83588         36.90         72.6         1.86739         39.44           62.7         1.80596         34.39         67.7         1.38500         36.96         72.7         1.36803         39.49           62.2         1.30577         34.44         67.8         1.33712         37.01         72.8         1.86687         39.54           62.9         1.30717         34.49         67.9         1.33774         37.06         72.9         1.36995         39.64           63.1         1.30887         34.65         68.2         1.38981         37.21         73.2         1.37124         39.7	61.9	1.80117	88.97	66.9	1.88155	36.55	71.9	1.36292	39.08
62.2         1.80297         34.18         67.2         1.83840         36.70         72.2         1.86488         39.24           62.3         1.30566         34.18         67.3         1.83402         36.75         72.3         1.86487         39.29           62.4         1.80416         34.28         67.4         1.83464         36.80         72.4         1.86611         39.34           62.5         1.80476         34.28         67.5         1.83526         36.85         72.5         1.86675         38.39           62.6         1.80536         34.84         67.6         1.83588         36.90         72.6         1.36789         39.44           62.7         1.80596         34.39         67.7         1.33650         36.96         72.7         1.36803         39.49           62.8         1.30657         34.44         67.8         1.33712         37.01         72.8         1.36867         39.54           62.9         1.30717         34.49         67.9         1.33774         37.06         72.9         1.86931         39.59           63.0         1.80877         34.54         68.0         1.83886         37.11         73.0         1.36995         39.6									
62.4         1.80416         34.28         67.4         1.83464         86.80         72.4         1.86611         39.34           62.5         1.80476         34.28         67.5         1.83526         36.85         72.5         1.86675         39.89           62.6         1.30536         34.34         67.6         1.33588         36.90         72.6         1.86739         39.44           62.7         1.80596         34.39         67.7         1.38630         36.96         72.7         1.36863         39.49           62.8         1.80657         34.44         67.8         1.33712         37.01         72.8         1.36867         39.54           62.9         1.30717         34.49         67.9         1.38774         87.06         72.9         1.86981         39.59           63.0         1.80777         34.54         68.0         1.38886         37.11         78.0         1.36995         39.64           63.1         1.30887         34.59         68.1         1.38889         37.16         78.1         1.37069         39.69           63.2         1.80897         34.65         68.2         1.38961         37.21         78.2         1.37124         39.7	62.2		34.13		1.33340				
62.5         1.80476         34.28         67.5         1.38526         36.85         72.5         1.86675         39.89           62.6         1.30536         34.34         67.6         1.33588         36.90         72.6         1.36739         39.44           62.7         1.30596         34.39         67.7         1.33650         36.96         72.7         1.36803         39.49           62.8         1.80657         34.44         67.8         1.33774         37.06         72.9         1.36981         39.59           62.9         1.80717         34.49         67.9         1.38774         37.06         72.9         1.36981         39.59           63.0         1.80777         34.54         68.0         1.38836         37.11         78.0         1.36995         39.69           63.1         1.30887         34.59         68.1         1.38899         37.16         78.1         1.37059         39.69           63.2         1.80897         34.65         68.2         1.38961         37.21         78.2         1.87124         39.74           63.3         1.30958         34.70         68.3         1.34023         37.26         78.3         1.87188         39.7								1.86547	
62.6         1.30536         34.34         67.6         1.33588         36.90         72.6         1.86739         39.44           62.7         1.30596         34.49         67.7         1.38650         36.96         72.7         1.36803         39.49           62.8         1.30657         34.44         67.8         1.33712         37.01         72.8         1.36867         39.54           62.9         1.30717         34.49         67.9         1.38774         87.06         72.9         1.36995         39.54           63.0         1.80777         34.54         68.0         1.33886         37.11         78.0         1.36995         39.64           63.1         1.30887         34.59         68.1         1.38899         37.16         78.1         1.37059         39.69           63.2         1.80897         34.65         68.2         1.33961         37.21         73.2         1.37124         39.74           63.3         1.30958         34.70         68.3         1.34023         37.26         78.3         1.37188         39.79           68.4         1.31018         34.80         68.5         1.34148         37.36         73.5         1.37317         39.9									
62.7         1.80596         34.39         67.7         1.38650         36.96         72.7         1.36803         39.49           62.8         1.30657         34.44         67.8         1.33712         37.01         72.8         1.36867         39.54           62.9         1.30717         34.49         67.9         1.33774         37.06         72.9         1.36981         39.59           68.0         1.80777         34.54         68.0         1.38886         37.11         78.0         1.36995         39.64           68.1         1.80887         34.59         68.1         1.38899         37.16         78.1         1.37059         39.69           68.2         1.80897         34.65         68.2         1.33961         37.21         78.2         1.37124         39.74           63.3         1.80958         34.70         68.8         1.34023         37.26         73.3         1.37188         39.79           68.4         1.31018         34.75         68.4         1.34085         37.31         78.4         1.37222         39.84           63.5         1.31139         34.80         68.5         1.34148         37.36         73.51         1.37317         39.									
62.9         1.30717         34.49         67.9         1.33774         87.06         72.9         1.36981         89.59           63.0         1.80777         34.54         68.0         1.38886         37.11         78.0         1.36995         89.64           68.1         1.30887         34.59         68.1         1.38899         37.16         78.1         1.37059         89.69           68.2         1.80897         34.65         68.2         1.38961         37.21         78.2         1.87124         89.74           68.3         1.80958         34.70         68.3         1.34023         37.26         73.3         1.87188         39.79           68.4         1.81018         34.75         68.4         1.34085         37.81         73.4         1.37252         39.84           68.5         1.31189         34.85         68.6         1.34148         37.30         78.5         1.37381         39.94           68.7         1.31199         34.90         68.7         1.34273         87.47         78.7         1.37446         39.99           68.8         1.31260         34.96         68.8         1.34385         37.52         78.8         1.37510         40.0					1.33650		72.7	1.36803	39.49
68.1         1.80887         34.59         68.1         1.83899         37.16         78.1         1.87059         39.69           68.2         1.80897         34.65         68.2         1.83891         37.21         78.2         1.87124         39.74           68.3         1.80958         34.70         68.3         1.34023         37.26         78.3         1.87188         39.79           68.4         1.81018         34.75         68.4         1.34085         37.31         78.4         1.37252         39.84           68.5         1.31189         34.85         68.6         1.34148         37.30         73.5         1.37317         39.89           68.6         1.31199         34.90         68.7         1.34273         37.47         78.7         1.37446         39.99           68.8         1.31260         34.96         68.8         1.34385         37.52         73.8         1.37510         40.04           68.9         1.31820         35.01         68.9         1.34398         37.57         73.9         1.37639         40.14           64.0         1.31381         35.06         69.0         1.34460         37.62         74.0         1.37639         40.1									
68.1         1.80887         34.59         68.1         1.83899         37.16         78.1         1.87059         39.69           68.2         1.80897         34.65         68.2         1.83891         37.21         78.2         1.87124         39.74           68.3         1.80958         34.70         68.3         1.34023         37.26         78.3         1.87188         39.79           68.4         1.81018         34.75         68.4         1.34085         37.31         78.4         1.37252         39.84           68.5         1.31189         34.85         68.6         1.34148         37.30         73.5         1.37317         39.89           68.6         1.31199         34.90         68.7         1.34273         37.47         78.7         1.37446         39.99           68.8         1.31260         34.96         68.8         1.34385         37.52         73.8         1.37510         40.04           68.9         1.31820         35.01         68.9         1.34398         37.57         73.9         1.37639         40.14           64.0         1.31381         35.06         69.0         1.34460         37.62         74.0         1.37639         40.1	63.0	1.30777	<b>84.54</b>	68.0	1.83836	87.11	78.0	1.36995	39,64
68.3         1.80958         34.70         68.8         1.34023         87.26         78.3         1.87188         39.79           68.4         1.31018         34.75         68.4         1.34085         37.31         78.4         1.37252         39.84           68.5         1.31078         34.80         68.5         1.34148         87.36         73.5         1.37317         39.89           63.6         1.31139         34.85         68.6         1.34210         37.41         78.6         1.37381         39.99           68.7         1.31199         34.90         68.7         1.34273         37.47         78.7         1.37446         39.99           68.8         1.31260         34.96         68.8         1.34385         37.52         78.8         1.37510         40.04           63.9         1.31820         35.01         68.9         1.34460         37.62         74.0         1.37639         40.14           64.1         1.31442         35.11         69.1         1.34523         37.72         74.1         1.37704         40.19           64.2         1.31502         36.16         69.2         1.34525         37.72         74.2         1.37788         40.2	68.1			68.1	1.83899	37.16	78.1	1.37059	39.69
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$									
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$									
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$							73.5	1.37317	39.89
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$									
68.9         1.31820         85.01         68.9         1.34898         87.57         73.9         1.37575         40.09           64.0         1.31381-35.06         69.0         1.34460         37.62         74.0         1.37639         40.14           64.1         1.31442         35.11         69.1         1.34523         37.67         74.1         1.37704         40.19           64.2         1.31502         35.16         69.2         1.34525         37.72         74.2         1.37768         40.24           64.3         1.31563         35.21         69.8         1.34648         37.77         74.8         1.37898         40.34           64.4         1.31624         35.27         69.4         1.34711         37.82         74.4*         1.37998         40.34           64.5         1.31684         35.32         69.5         1.34774         37.87         74.6         1.38027         40.49           64.6         1.31745         35.37         69.6         1.34836         37.92         74.6         1.38002         40.49           64.8         1.31867         35.47         69.8         1.34962         38.02         74.8         1.38157         40.54									
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		1.31320	85.01	68.9		87.57			
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$						1			
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$								1.37704	
64.4     1.81624     85.27     69.4     1.84711     87.82     74.4*     1.87898     40.34       64.5     1.31684     85.32     69.5     1.34774     87.87     74.5     1.37962     40.89       64.6     1.31745     35.37     69.6     1.34836     37.92     74.6     1.38027     40.44       64.7     1.31806     35.42     69.7     1.34893     37.97     74.7     1.38092     40.49       64.8     1.31867     35.47     69.8     1.34962     38.02     74.8     1.38157     40.54	64.3	1.31563	35.21	69.8					
64.6     1.31745     35.37     69.6     1.34836     37.92     74.6     1.38027     40.44       64.7     1.31806     35.42     69.7     1.34899     37.97     74.7     1.38092     40.49       64.8     1.31867     35.47     69.8     1.34962     38.02     74.8     1.38157     40.54									
64.7     1.31806     35.42     69.7     1.34899     37.97     74.7     1.38092     40.49       64.8     1.31867     35.47     69.8     1.34962     38.02     74.8     1.38157     40.54									
64.8   1.31867   35.47   69.8   1.34962   38.02   74.8   1.38157   40.54							74.7		
64.9   1.81928   85.52    69.9   1.85025   88.07    74.9   1.88222   40.59					1.34962	38.02	74.8	1.38157	40.54
	64.9	1.81928	85.52	69.9	1.85025	38.07	74.9	1.38222	40.59

APPENDIX.

# Comparison between Specific Gravity Figures, Degree Baumé and Degree Brix.—Continued.

Percentage of sugar ac- cording to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar ac- cording to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar ac- cording to Balling or degree Brix.	Specific gravity.	Degree Baumé.
75.0 75.1 75.2 75.3 75.4 75.5 75.6 75.7 75.8	1.38287 1.38352 1.38417 1.38482 1.38547 1.38612 1.38677 1.38743 1.38808 1.38873	40.64 40.69 40.74 40.79 40.84 40.89 40.94 40.99 41.04 41.09	80.0 80.1 80.2 80.3 80.4 80.5 80.6 80.7 80.8 80.9	1.41586 1.41658 1.41720 1.41787 1.41854 1.41921 1.41989 1.42056 1.42128 1.42190	43.11 43.61 43.21 43.26 43.31 43.36 43.41 43.45 43.50 43.55	85.0 85.1 85.2 85.3 85.4 85.5 85.6 85.7 85.8	1.44986 1.45055 1.45124 1.45198 1.45262 1.45831 1.45401 1.45470 1.45589 1.45609	45.54 45.59 45.64 45.69 45.74 45.78 45.88 45.88 45.98
76.0 76.1 76.2 76.3 76.4 76.5 76.6 76.7 76.8 76.9	1.88989 1.89004 1.89070 1.89185 1.89201 1.89266 1.89882 1.39397 1.89463 1.39529	41.14 41.19 41.24 41.20 41.33 41.38 41.48 41.48 41.53 41.58	81.0 81.1 81.2 81.3 81.4 81.5 81.6 81.7 81.8	1.42258 1.42825 1.42898 1.42460 1.42528 1.42595 1.42663 1.42781 1.42798 1.42866	43.60 43.65 43.70 43.75 43.80 43.85 43.89 43.94 43.99 44.04	86.0 86.1 86.2 86.3 86.4 86.5 86.6 86.7 86.8 86.9	1.45678 1.45748 1.45817 1.45887 1.46026 1.46026 1.46165 1.46235 1.46304	46.02 46.07 46.12 46.17 46.22 46.26 46.31 46.86 46.41 46.40
77.0 77.1 77.2 77.3 77.4 77.6 77.6 77.7 77.8	1.89595 1.89660 1.89726 1.39792 1.39858 1.39924 1.89990 1.40056 1.40122 1.40188	41.68 41.68 41.78 41.78 41.83 41.88 41.93 42.03 42.08	82.0 82.1 82.2 82.3 82.4 82.5 82.6 82.7 82.8 82.9	1.42934 1.43002 1.43070 1.43137 1.43205 1.43273 1.43841 1.43409 1.43478 1.43546	44.09 44.14 44.19 44.24 44.28 44.33 44.38 44.48 44.48	87.0 87.1 87.2 87.3 87.4 87.5 87.6 87.7 87.8 87.9	1.46374 1.46444 1.46514 1.46584 1.46654 1.46724 1.46794 1.40864 1.46934 1.47004	46.50 46.55 46.60 46.65 46.69 46.74 46.79 46.84 46.88 46.93
78.0 78.1 78.2 78.3 78.4 78.5 78.6 78.7 78.8 78.8	1.40254 1.40321 1.40387 1.40453 1.40520 1.40586 1.40652 1.40719 1.40785 1.40852	42.18 42.28 42.28 42.32 42.37 42.42 42.47 42.52 42.57	83.0 83.1 83.2 83.3 83.4 83.5 83.6 83.7 83.8 83.9	1.43614 1.43682 1.43750 1.43819 1.43887 1.43955 1.44024 1.44092 1.44161 1.44229	44.58 44.62 44.67 44.72 44.77 44.82 44.87 44.91 44.96 45.01	88.0 88.1 88.2 88.3 88.4 88.5 88.6 88.7 88.8 88.9	1.47074 1.47145 1.47215 1.47285 1.47856 1.47426 1.47496 1.47567 1.47637 1.47708	46.98 47.03 47.08 47.12 47.17 47.22 47.27 47.31 47.36 47.41
79.0 79.1 79.2 79.3 79.4 79.5 79.6 79.7 79.8 79.9	1.40918 1.40985 1.41052 1.41118 1.41185 1.41252 1.41818 1.41885 1.41452 1.41519	42.62 42.67 42.72 42.77 42.82 42.87 42.92 42.96 43.01 43.06	84.0 84.1 84.2 84.3 84.4 84.5 84.6 84.7 84.8 84.9	1.44298 1.44367 1.44435 1.44578 1.44578 1.44641 1.44710 1.44779 1.44848 1.44917	45.06 45.11 45.16 45.21 45.25 45.30 45.35 45.40 45.45 45.49	89.0 89.1 89.2 80.3 89.4 89.5 89.6 89.7 89.8 89.9	1.47778 1.47849 1.47920 1.47991 1.48061 1.48132 1.48203 1.48274 1.48345 1.48416	47.46 47.50 47.55 47.60 47.65 47.69 47.74 47.79 47.83 47.88

Comparison between Specific Gravity Figures, Degree Baumé and Degree Brix.—Continued.

					<del></del>			<del> </del>
Percentage of sugar ac- cording to Balling or degree Brix.	Specific gravity.	Degree Baumé,	Percentage of sugar ac- cording to Balling or degree Brix.	Specific gravity.	Degree Baumé.	Percentage of sugar ac- cording to Balling or degree Brix.	Specific gravity.	Degree Baumé.
90.0	1.48486	47.93	94.0	1.51859	49.81	98.0	1.54290	51.65
90.1	1.48558	47.98	94.1	1.51431	49.85	98.1	1.54365	51.70
90.2	1.48629	48.02	94.2	1.51504	49.90	98.2	1.54440	51.74
90.8	1.48700	48.07	94.3	1.51577	49.94	98.3	1.54515	51.79
90.4	1.48771	48.12	94.4	1.51649	49.99	98.4	1.54590	51.83
90.5	1.48842	48.17	94.5	1.51722	50.04	98.5	1.54665	51.88
90.6	1.48913	48.21	94.6	1.51795	50.08	98.6	1.54740	51.92
90.7	1.48985	48.26	94.7	1.51868	50.13	98.7	1.54815	51.97
90.8	1.49056	48.31	94.8	1.51941	50.18	98.8	1.54890	52.01
90.9	1.49127	48.35	94.9	1.52014	50.22	98.9	1.54965	52.06
1			[]	ļ		ļ		
91.0	1.49199	48.40	95.0	1.52087	50.27	99.0	1.55040	52.11
91.1	1.49270	48.45	95.1	1.52159	50.32	99.1	1.55115	52.15
91.2	1.49342	48.50	95.2	1.52232	50.36	99.2	1.55189	52.20
91.3	1.49418	48.54	95.3	1.52304	50.41	99.8	1.55264	52.24
91.4	1.49485	48.59	95.4	1.52376	50.45	99.4	1.55338	52.29
91.5	1.49556	48.64	95.5	1.52449	50.50	99.5	1.55413	52.38
91.6	1.49628	48.68	95.6	1.52521	50.55	99.6	1.55487	52.38
91.7	1.49700	48.73	95.7	1.52593	50.59	99.7	1.55562	52.42
91.8	1.49771	48.78	95.8	1.52665	50.64	99.8	1.55686	52.47
91.9	1.49848	48.82	95.9	1.52738	50.69	99.9	1.55711	52.51
1								
92.0	1.49915	48.87	96.0	1.52810	50.73	100.0	1.55785	52.56
92.1	1.49987	48.92	96.1	1.52884	50.78		,	
92.2	1.50058	48.96	96.2	1.52958	50.82			
92.3	1.50130	49.01	96.8	1.53032	50.87	Į.		
92.4	1.50202	49.06	96.4	1.53106	50.92			
92.5	1.50274	49.11	96.5	1.53180	50.96			
92.6	1.50846	49.15	96.6	1.58254	51.01	Į .	1	1
92.7	1.50419	49.20	96.7	1.53828	51.05	ļ	1	
92.8	1.50491	49.25	96.8	1.53402	51.10		ļ	
92.9	1.50568	49.29	96.9	1.53476	51.15		ļ	
00.0								
98.0	1.50633	49.84	97.0	1.53550	51.19			
93.1	1.50707	49.39	97.1	1.53624	51.24			
93.2	1.50779	49.48	97.2	1.53698	51.28	Į		
93.3	1.50852	49.48	97.3	1.53772	51.33	1		l .
98.4	1.50924	49.58	97.4	1.53846	51.38	]		
93.5 93.6	1.50996	49.57	97.5	1.58920	51.42	Į į		
98.6	1.51069 1.51141	49.62	97.6	1.58994	51.47	! i		
98.8	1.51214	49.67 49.71	97.7 97.8	1.54068 1.54142	51.51	(		
98.9	1.51286	49.76	97.9	1.54142	51.56 51.60	1 . 1		1
]	1.01200	20.10	01.0	1.02410	01.00		1	
<u> </u>	<del>!</del>			!		<u> </u>		1

APPENDIX.

## 6. Table of Weight and Volume Relations.

r					
_	Specific	Specific volume	Weight of 1	Volume in U. S.	Weight of
Degrees Baumé.	gravity 25° C.	(volume of	U.S. gallon in	gallons of 100	1 fluidounce in
Daume.	25° C.	1 kilogram in liters).*	pounds avoirdupois.+	lbs. avoirdupois.;	grains.
	20 0.			i	
70	0.700	1.4286	5.819	17.185	318.2
67	0.710	1.4085	5.902	16.943	322.8
64.5	0.720	1.3889	5.985	16.707	327.3
61.8	0.730	1.3699	6.068	16.479	331.9
59	0.740	1.3514	6.151	16.256	336.4
56.5	0.750	1.3333	6.235	16.039	341
54	0.760	1.3158	6.318	15.828	345.5
51.8	0.770	1.2987	6.401	15.623	350
49.5	0.780	1.2821	6.484	15.422	354.6
47	0.790	1.2658	6.567	15.227	359.1
45	0.800	1.2500	6.650	15.037	363.7
43	0.810	1.2346	6.733	14.851	368.2
41	0.820	1.2195	6.817	14.670	372.8
38.8	0.830	1.2049	6.900	14.494	377.3
36.8	0.840	1.1905	6.983	14.321	381.9
34.8	0.850	1.1765	7.066	14.152	386,4
33	0.860	1.1628	7.149	13.988	391
31	0.870	1.1494	7.232	13.827	395.5
29	0.880	1.1364	7.315	13.670	400.1
27.7	0.890	1.1236	7.398	13,516	404.6
25.5	0.900	1.1111	7.481	13.366	409.1
24	0.910	1.0989	7.565	13.219	413.7
22	0.920	1.0870	7.648	13.075	418.2
20.5	0.930	1.0753	7.731	12.935	422.8
19	0.940	1.0638	7.814	12.797	427.3
17.5	0.950	1.0526	7.897	12.663	431.9
15.5	0.960	1.0417	7.980	12.531	436.4
14.2	0.970	1.0309	8.063	12.401	441
13	0.980	1.0204	8.147	12.275	445.5
11.5	0.990	1.0101	8.230	12.151	450.1
10	1.000	1.0000	8.313	12.029	454.6
3	1.020	0.9804	8.479	11.794	463.7
5.7	1.040	0.9615	8.645	11.567	472.8
8.6	1.060	0.9434	8,812	11.348	481.9
10.5	1.080	0.9259	8.978	11.138	491
13	1.100	0.9091	9.144	10.936	500.1
16	1.120	0.8929	9.310	10.741	509.2
17.6	1.140	0.8772	9.477	10.552	518.3
20	1.160	0.8621	9.643	10.370	527.4
22	1.180	0.8475	9.809	10.194	536.4
24	1.200	0.8333	9.975	10.025	545,5
26.5	1.220	0.8197	10.142	9.860	554.6
28	1.240	0.8065	10.308	9.701	563.7
29.8	1.260	0.7937	10.474	9.547	572.8
31.6	1.280	0.7813	10.640	9.398	581.9
34	1.300	0.7692	10.807	9.253	591.0
35.2	1.320	0.7576	10.973	9.113	600.1
36.8	1.340	0.7463	11.139	8.977	609.2
38	1.360	0.7353	11.305	8.845	618.3
39.6	1.380	0.7246	11.472	8.717	627.4
41	1.400	0.7143	11.638	8.592	636.4
43	1.420	0.7042	11.804	8.471	645.5
44	1.440	0.6944	11.970	8.354	654.6
45.5	1.460	0.6849	12.137	8.239	663.7
47	1.480	0.6757	12.303	8.128	672.8
48	1.500	0.6667	12.469	8.020	681,9
49.5	1.520	0.6579	12.635	7.914	691.0
51	1.540	0.6494	12.802	7.811	700.1

APPENDIX.

Table of Weight and Volume Relations.—Continued.

Degrees Baumé.	Specific gravity 25° C. 25° C.	Specific volume (volume of 1 kilogram in liters).*	Weight of 1 U. S. gallon in pounds avoirdupois.†	Volume in U. S. gallons of 100 lbs. avoirdupois.;	Weight of 1 fluidounce in grains.
52 53.4 54.4 55.4 56.6 58 59 60 61 61.7 62.8 63.5 64.2 65.1 66 67.6 68.7 69.5 70.5	1.560 1.580 1.600 1.620 1.640 1.660 1.700 1.720 1.740 1.760 1.780 1.800 1.820 1.840 1.860 1.880 1.900	0.6410 0.6329 0.6250 0.6173 0.6098 0.6025 0.5952 0.5882 0.5814 0.5747 0.5682 0.5618 0.5556 0.5495 0.5495 0.5485 0.5376 0.5319 0.5263	12.968 13.134 13.300 13.467 13.633 13.799 13.966 14.132 14.298 14.464 14.631 14.797 14.963 15.129 15.296 15.462 15.628 15.794 15.961	7.711 7.614 7.519 7.426 7.335 7.247 7.160 7.076 6.994 6.913 6.835 6.758 6.683 6.610 6.538 6.467 6.399 6.331 6.265	709.2 718.3 727.4 736.5 745.6 754.6 763.7 772.8 781.9 791.0 800.1 809.2 818.3 827.4 836.5 845.6 854.7 863.8 872.8
71.2 72 73 74	1.940 1.960 1.980 2.000	0.5155 0.5102 0.5051 0.5000	16.127 16.293 16.459 16.626	6.201 6.137 6.075 6.015	881.9 891.0 900.1 909.2

<sup>\*</sup>Or of 1 gram in cubic centimeters; strictly true only at 0° C. in vacuo.
† Multiply these figures by 2 for weight of one U. S. pint in ounces avoirdupois.
‡ Divide these figures by 2 for volume in pints of 100 ounces avoirdupois.

IV. Alcohol Tables.

Percentage of Alcohol by Weight and by Volume from the Specific Gravity (at 15.5° C.), by Otto Hehner.

		·						
G.,,,,,,	Percent-	Percent-		Percent-	Percent-		Percent-	Percent-
Specific	age of	age of	Specific	age of	age of	Specific	age of	age of
gravity at 15.5° C.	absolute	absolute alcohol by	gravity at 15.5° C.	absolute alcohol by	i ardsomite i	grāvity at 15.5° C.	absolute	absolute
20.0 0.	weight.	volume.	10,0-0,	weight.	alcohol by volume.	10.5° C.	weight.	alcohol by
		70111101		THE CARLO	VOIUME.	·	Weight.	
1.0000	0.00	0.00						
0.9999	0.05	0.07	0.9949	2.89	3.62	0.000	204	740
8	0.11	0.13				0.9899	5.94	7.40
			8	2.94	3.69	8	6.00	7.48
7	0.16	0.20	7	8.00	3.76	7	6.07	7.57
6	0.21	0.26	6	3.06	8.83	(6	6.14	7.66
5	0.26	0.88	5	3.12	8.90	5	6.21	7.74
4	0.82	0.40	4	8.18	3.98	4	6.28	1 7.83
8	0.37	0.46	8	8.24	4.05	1 8	6.36	7.92
2	0.42	0.58	2	3.29	4.12	1 2	6.43	8.01
1	0.47	0.60	1	3.35	4.20	ī	6.50	8.10
0	0.58	0.66	Õ	3.41	4.27	Ō	6.57	8.18
0.9989	0.58	0.78	0.9989	3.47	4.84	0.9889	6.64	8.27
8	0.68	0.79	8	3.58	4.42	8	6.71	8.36
7	0.68	0.86	7	8.59	4.49	7	6.78	8.45
6	0.74	0.93	6	3.65	4.56	6	6.86	8.54
5	0.79	0.99	5	8.71	4.68	5	6.98	8.63
4	0.84	1.06	. 4	8.76	4.71	4	7.00	8.72
8	0.89	1.18	8	3.82	4.78	8	7.07	8.80
2	0.95	1.19	2	3.88	4.85	2	7.13	8.88
1	1.00	1.26	1	3.94	4.93	1	7.20	8.96
0	1.06	1.34	0	4.00	5.00	0	7.27	9.04
0.9979	1.12	1.42	0.9929	4.06	5.08	0.9879	7.88	9.18
8	1.19	1.49	8	4.12	5.16	8	7.40	9.21
. 7	1.25	1.57	7	4.19	5.24	7	7.47	9.29
	1.25	1.65	6	4.25	5.82	6	7.58	9.37
6		1.73	5	4.81		5	7.60	9.45
5	1.37				5.39			
4	1.44	1.81	4	4.87	5.47	4	7.67	9.54
8	1.50	1.88	8	4.44	5.55	8	7.78	9.62
2	1.56	1.96	2	4.50	5.63	2	7.80	9.70
1	1.62	2.04	1	4.56	5.71	1	7.87	9.78
0	1.69	2.12	0	4.62	5.78	0	7.93	9.86
0.9969	1.75	2.20	0.9919	4.69	5.86	0.9869	8.00	9.95
8	1.81	2.27	8	4.75	5.94	8	8.07	10.03
7	1.87	2.85	7	4.81	6.02	7	8.14	10.12
6	1.94	2.48	6	4.87	6.10	6	8.21	10.21
5	2.00	2.51	5	4.94	6.17	5	8.29	10.80
4	2.06	2.58	4	5.00	6.24	4	8.36	10.38
			3	5.06		8	8.48	10.47
3	2.11	2.62	2		6.32	2		10.56
2	2.17	2.72		5.12	6.40		8.50	
1	2.22	2.79	1	5.19	6.48	1	8.57	10.65
0	2.28	2.86	0	5.25	6.55	0	8.64	10.78
0.9959	2.83	2.93	0.9909	5.81	6.63	0.9859	8.71	10.82
8	2.89	8.00	8	5.87	6.71	8	8.79	10.91
7	2.44	3.07	7	5.44	6.78	7	8.86	11.00
6	2.50	8.14	6	5.50	6.86	6	8.93	11.08
5	2.56	3.21	5	5.56	6.94	5		11.17
4	2.61	3.28	4	5.62	7.01	4		11.26
3	2.67	8.35	∥ ŝ	5.69	7.09	3		11.35
2	2.72	3.42	2	5.75	7.17			11.44
ĺ	2.78	3.49	î	5.81	7.25	ī		11.52
Ô	2.83	3.55	Ô	5.87	7.32	l ô		11.61
, ,	2.00	1 0.00	11	1 0.01	1	11 0	1 011111	,

Percentage of Alcohol by Weight and by Volume from the Specific Gravity (at 15.5° C.), by Otto Hehner.—Continued.

Specific gravity at 15.5° C.	Percentage of absolute alcohol by weight.	Percent- age of absolute alcohol by volume.	Specific gravity at 15.5° C.	Percent- age of absolute alcohol by weight.	Percent- age of absolute alcohol by volume.	Specific gravity at 15.5° C.	Percent- age of absolute alcohol by weight.	Percent- age of absolute alcohol by volume.
0.9849	9.43	11.70	0.9799	13.23 13.31	16.33 16.43	0.9749	17.83 17.42	21.29 21.39
8 7	9.50 9.57	11.79 11.87	8 7	13.38	16.52	7	17.50	21.49
6	9.64	11.96	6	13.46	16.61	6	17.50	21.49
5	9.71	12.05	5	13.54	16.70	5	17.67	21.69
4	9.79	12.13	4	13.62	16.80	4	17.75	21.79
8	9.86	12.22	3	13.69	16.89	3	17.83	21.89
2	9.93	12.81	2	13.77	16.98	. 2	17.92	21.99
1	10.00	12.40	1	13.85	17.08	1	18.00	22.09
0	10.08	12.49	0	13.92	17.17	0	18.08	22.18
0.9889	10.15	12.58	0.9789	14.00	17.26	0.9739	18.15	22.27
8	10.23	12.68	8	14.09	17.37	8	18.23	22.86
7	10.31	12.77	7	14.18	17.48	7	18.31	22.46
6	10.38	12.87	6	14.27	17.59	6	18.38	22.55
5	10.46	12.96	5	14.36	17.70	5	18.46	22.64
4	10.54	13.05	4	14.45	17.81	4	18.54	22.73
8 2	10.62	13.15	3	14.55	17.92	8	18.62	22.82
1	10.69	13.24	2	14.64	18.03	2	18.69	22.92
0	10.77	18.84	1	14.73	18.14	1 0	18.77	28.01
· ·	10.85	13.43	0	14.82	18.25		18.85	23.10
0.9829	10.92 11.00	13.52 13.62	0.9779	14.90 15.00	18.36	0.9729	18.92	23.19
7			7	15.08	18.48	8	19.00	28.28
6	11.08 11.15	13.71 13.81	6	15.17	18.58 18.68	7 6	19.08 19.17	23.38 23.48
5	11.23	13.90	5	15.25	18.78	5	19.17	23.58
4	11.31	13.99	4	15.33	18.88	4	19.33	23.68
ŝ	11.38	14.09	3	15.42	18.98	3	19.42	23.78
2	11.46	14.18	2	15.50	19.08	2	19.50	23.88
1	11.54	14.27	1	15.58	19.18	l ī	19.58	23.98
0	11.62	14.87	0	15.67	19.28	0	19.67	24.08
0.9819	11.69	14.46	0.9769	15.75	19.39	0.9719	19.75	24.18
8	11.77	14.56	8	15.83	19.49	8	19.83	24.28
7	11.85	14.65	7	15.92	19.59	7	19.92	24.38
6	11.92	14.74	6	16.00	19.68	6	20.00	24.48
. 5	12.00	14.84	5	16.08	19.78	5	20.08	24.58
4	12.08	14.98	4	16.15	19.87	4	20.17	24.68
8	12.15	15.02	8	16.23 16.31	19.96	3	20.25	24.78
2   1	$12.23 \\ 12.31$	15.12 15.21	$\begin{bmatrix} 2 \\ 1 \end{bmatrix}$	16.38	$20.06 \\ 20.15$	$egin{array}{c} 2 \\ 1 \end{array}$	20.33 20.42	24.88
, 9	12.88	15.30	ō	16.46	20.15	ō	20.50	$24.98 \\ 25.07$
0.9809	12.46	15.40	0.9759	16.54	20.33	0.9709	20.58	05 17
8	12.54	15.49	8	16.62	20.43	8	20.67	25.17 25.27
7	12.62	15.58	7	16.69	20.52	7	20.75	25.37
6 1	12.69	15.68	6	16.77	20.61	6	20.83	25.47
. 5	12.77	15.77	5	16.85	20.71	5	20.92	25.57
4	12.85	15.86	4	16.92	20.80	4	21.00	25.67
	12.92	15.96	3	17.00	20.89	8 (	21.08	25.76
3			ام					
2	13.00	16.05	2	17.08	20.99	2	21.15	25.86
3 2 1 0	13.00 13.08 18.15	16.05 16.15 16.24	1 0	17.08 17.17 17.25	21.09 21.19	1 0	21.18 21.28 21.81	25.86 25.95 26.04

Percentage of Alcohol by Weight and by Volume from the Specific Gravity (at 15.5° C.), by Otto Hehner.—Continued.

Specific gravity at 15.5° C.	Percent- age of absolute alcohol by weight.	Percent- age of absolute alcohol by volume.	Specific gravity at 15.5° C.	Percent- age of absolute alcohol by weight.	Percent- age of absolute alcohol by volume.	Specific gravity at 15.5° C.	Percent- age of absolute alcohol by weight.	Percent- age of absolute alcohol by volume.
0.9699	21.38	26.13	0.9649	25.21	80.65	0.9599	28.62	34.61
8	21.46	26.22	8	25.29	30.73	8	28.69	34.69
1 7	21.54	26.31	7	25.36	30.82	7	28.75	34.76
6	21.62	26.40	6	25.43	30.90	6	28.81	84.83
5	21.69	26.49	5	25.50	30.98	5	28.87	34.90
4	21.77	26.58	4	25.57		4	28.94	34.97
3	21.85	26.67	3		31.07	3		
2	21.92	26.77	2	25.64	81.15		29.00	35.05
				25.71	31.23	2	29.07	35.12
1	22.00	26.86	1	25.79	31.32	1	29.13	35.20
0	22.08	26.95	0	25.86	81.40	0	29.20	85.28
0.9689	22.15	27.04	0.9639	25.93	31.48	0.9589	29.27	35.35
8	22.23	27.13	8	26.00	31.57	8	29.33	85.43
7	22.31	27.22	7	26.07	31.65	7	29.40	85.51
6	22.38	27.81	6					
				26.13	81.72	6	29.47	35.58
5	22.46	27.40	5	26.20	31.80	5	29.53	35.66
4	22.54	27.49	4	26.27	31.88	4	29.60	35.74
8	22.62	27.59	8	26.33	31.96	3	29.67	35.81
2	22.69	27.68	2	26.40	32.03	2	29.73	85.89
1	22.77	27.77	1	26.47	32.11	1	29.80	35.97
0	22.85	27.86	0	26.53	82.19	0	29.87	36.04
0.9679	22.92	27.95	0.9629	26.60	32.27	0.9579	29.93	36.12
8	23.00	28.04	8	26.67	32.34	8	30.00	36.20
7	23.08	28.13	7			7	30.06	36.26
				26.78	32.42			
6	28.15	28.22	6	26.80	32.50	6	30.11	36.32
5	23.23	28.31	5	26.87	32.58	5	30.17	36.39
4	23.31	28.41	4	26.93	32.65	4	30.22	36.45
8	23.38	28.50	8	27.00	32.73	3	30.28	86.51
2	23.46	28.59	2	27.07	32.81	2	30.33	36.57
1	23.54	28.68	1	27.14	32.90	1	30.39	36.64
0	23.62	28.77	0	27.21	32.98	0	80.44	36.70
0.9669	23.69	28.86	0.9619	27.29	88.06	0.9569	30.50	36.76
8	23.77	28.95	8	27.36	33.15	8	30.56	36.83
7	23.85	29.04	7	27.43		7		36.89
					33.23		30.61	
6	23.92	29.13	6	27.50	88.81	6	80.67	86.95
5	24.00	29.22	5	27.57	33.89	5	30.72	37.02
4	24.08	29.31	4	27.64	83.48	4	30.78	37.08
8	24.15	29.40	3	27.71	33.56	3	30.83	87.14
2	24.23	29.49	2	27.79	33.64	2	30.89	37.20
1	24.31	29.58	1	27.86	33.73	1	30.94	37.27
0	24.88	29.67	0	27.98	83.81	0	31.00	37.3 <b>4</b>
0.0050	04.40	20.50		20.00			04.00	0
0.9659	24.46	29.76	0.9609	28.00	33.89	0.9559	81.06	37.41
8	24.54	29.86	8	28.06	38.97	8	31.12	37.48
7	24.62	29.95	7	28.12	34.04	7	31.19	37.55
6	24.69	30.04	6	28.19	84.11	6	31.25	37.62
5	24.77	30.13	5	28.25	34.18	5	81.81	37.69
4	24.85	30.22	4	28.31	84.25	4	81.37	37.76
3	24.92	80.81	3	28.37	34.33	8	31.44	37.83
2	25.00	30.40	2	28.44	34.40	2	31.50	37.90
1	25.07	30.48	1	28.50	34.47	1	31.56	37.97
ō	25.14	30.57	Ō	28.56	34.54	Ō	31.62	38.04
" 1			ı			ı		55.01
		1	I	•	, 1	ı	I	I

Percentage of Alcohol by Weight and by Volume from the Specific Gravity (at 15.5° C.), by Otto Hehner.—Continued.

	· · · ·	`						
Specific gravity at 15.5° C.	Percent- age of absolute alcohol by weight.	Percent- age of absolute alcohol by volume.	Specific gravity at 15.5° C.	Percentage of absolute alcohol by weight.	Percent- age of absolute alcohol by volume.	Specific gravity at 15.5° C.	Percent- age of absolute alcohol by weight.	Percen age of absolut alcohol volume
0.9549 8 7 6 5 4 8 2 1 0	81.69 81.75 81.81 81.87 81.94 82.00 82.06 82.12 82.19 82.25	38.18 38.25 38.33 38.40 38.47 38.53 38.60 88.68 38.75	0.9499 8 7 6 5 4 8 2 1	84.57 34.62 34.67 34.71 34.76 34.81 34.86 34.90 34.95 35.00	41.37 41.42 41.48 41.58 41.68 41.69 41.74 41.79 41.84	0.9449 87 65 4 8 2 1	87:17 87:22 37.28 87.33 87.39 87.44 87.50 87.56 87.61	44.24 44.30 44.36 44.43 44.49 44.55 44.61 44.67 44.73 44.79
0.9539 8 7 6 5 4 8 2 1	82.31 32.37 32.44 82.50 82.56 82.62 82.69 82.75 82.81 82.87	38.82 38.89 38.96 39.04 39.11 39.18 39.25 39.40 39.47	0.9489 8 7 6 5 4 3 2 1	85.05 85.10 85.15 85.20 85.25 85.30 85.35 85.40 85.45 35.50	41.90 41.95 42.01 42.06 42.12 42.17 42.28 42.29 42.34 42.40	0.9489 8 76 5 4 3 2 1	87.72 37.78 37.83 37.89 37.94 38.00 88.06 38.11 38.17 38.22	44.86 44.92 44.98 45.04 45.10 45.16 45.22 45.28 45.84 45.41
0.9529 8 7 6 5 4 3 2 1	82.94 83.00 83.06 83.12 83.18 83.24 83.29 83.35 83.41	89.54 39.61 39.68 39.74 89.81 39.87 39.94 40.01 40.07 40.14	0.9479 8 7 6 5 4 8 2	<b>85.55</b> 35.60 35.65 35.70 35.75 35.80 35.85 85.90 35.95 86.00	42.45 42.51 42.56 42.62 42.67 42.78 42.78 42.84 42.89 42.95	0.9429 8 7 6 5 4 3 2 1	38.28 38.33 38.39 38.44 38.50 38.56 38.61 38.67 38.72 38.78	45.47 45.53 45.59 45.65 45.71 45.77 45.83 45.89 45.95 46.02
0.9519 8 7 6 5 4 8 2 1 0	88.58 83.59 83.65 83.71 83.76 83.82 83.88 83.94 84.00 34.05	40.20 40.27 40.34 40.40 40.47 40.53 40.60 40.67 40.74 40.79	0.9469 8 7 6 5 4 3 2 1	36.06 36.11 36.17 36.22 36.28 36.39 36.44 36.50 36.56	48.01 48.07 48.13 48.19 48.26 48.82 43.38 48.44 48.50 48.56	0.9419 8 7 6 5 4 3 2 1	38.89 38.94 39.00 89.05 89.10 39.15 39.20 39.25 39.30	46.08 46.14 46.20 46.26 46.32 46.37 46.42 46.48 46.53 46.59
0.9509 8 7 6 5 4 3 2 1 0	84.10 84.14 84.19 84.24 84.29 84.83 84.88 84.48 84.48 84.52	40.84 40.90 40.95 41.00 41.05 41.11 41.16 41.21 41.26 41.32	0.9459 8 7 6 5 4 8 2 1	86.61 36.67 86.72 86.78 86.88 86.89 86.94 87.00 87.06 87.11	43.63 43.69 43.75 43.81 43.87 43.93 44.00 44.06 44.12 44.18	0.9409 8 7 6 5 4 8 2 1	89.35 89.40 89.45 89.55 89.60 89.65 89.70 89.75 89.80	46.64 46.70 46.75 46.80 46.86 46.97 47.02 47.08 47.18

Percentage of Alcohol by Weight and by Volume from the Specific Gravity (at 15.5° C.), by Otto Hehner.—Continued.

Percent- age of	Percent- age of	Specific	Percent- age of	Percent-	Specific	Percent- age of	Percent age of
absolute	absolute	gravity at	absolute	absolute	gravity at 15.5° C.	absolute alcohol by	absolute
weight.	volume.	20,0 0.	weight.	volume.		weight.	volume
39.85	47.18	0.9349	42.33	49.86	0.9299	44.68	52.34
39.90		8	42.38				52.39
					1		52.44 52.48
							52.53
					4		52.58
40.15	47.51	3	42.62	50.16	3	44.96	52.63
40.20	47.56		42.67	50.21		45.00	52.68
							52.72
40.80	47.67	0	42.76	50.81		45.09	52.77
40.35	47.72	0.9339	42.81	50.87	0.9280	45.55	58.24
							53.72
							54.19 54.66
					1		55.13
		4	43.05		80	47.82	55.60
40.65	48.05	8	43.10	50.67	20	48.27	56.07
40.70	48.10		43.14	50.72	10	48.78	56.54
					00	49.16	56.98
40.80	48.21	U	48.24	50.82			
40.85	48.26	0.9329	43.29	50.87	0.9190	49.64	57.45
40.90							57.92
							58.36 58.80
							59.22
		4		51.12	40	51.79	59.63
41.15	48.59	3	43.57	51.17	80	52.23	60.07
41.20	48.64		43.62				60.52
41.25 41.30	48.70 48.75	0	43.67 43.71	51.27 51.32	00	58.18	60.97 61.40
							04.04
							61.84 62.31
							62.79
		6		51.58	60	55.41	63.24
41.55	49.02	5	43.95	51.58	50	55.86	63.69
41.60	49.07	4	44.00	51.63	40	56.32	64.14
							64.58
							65.01 65.41
41.80	49.29	ō	44.18	51.82	00	58.05	65.81
41.0	40.04	0.000	44.00	F1 0F	0 0000	50 50	00 00
							66.69
		11					67.11
42.00	49.50	∭ 6	44.36	52.01	60	59.83	67.53
42.05	49.55	5	44.41	52.06	50	60.26	67.93
42.10	49.61				40		68.33
				52.15			68.72
		11 2					69.50
42.24	49.76	1	44.59	52.25	10	61.92	1 09.00
	age of absolute alcohol by weight.  39.85 39.95 40.00 40.05 40.10 40.25 40.30  40.35 40.40 40.45 40.50 40.45 40.65 40.70 40.75 40.80  40.85 41.00 41.05 41.10 41.15 41.20 41.25 41.30  41.85 41.40 41.55 41.60 41.55 41.60 41.55 41.80  41.85 41.95 42.00 42.05	age of absolute alcohol by weight.  39.85 39.90 39.95 47.18 39.95 47.29 40.00 47.35 40.05 47.40 40.10 47.45 40.15 47.62 40.30 47.66 40.25 47.67  40.35 47.67  40.35 47.72 40.40 47.78 40.45 47.83 40.55 47.83 40.55 47.99 40.65 40.70 40.75 48.10 40.75 48.10 40.75 48.10 40.80 48.21  40.85 48.26 40.90 48.82 40.95 48.87 41.00 48.83 41.10 48.84 41.15 41.25 48.70 41.30 48.75 41.35 48.80 41.40 48.86 41.45 48.91 41.55 41.20 48.86 41.45 48.91 41.55 41.20 48.86 41.45 48.91 41.55 41.20 48.86 41.45 48.91 41.55 49.02 41.60 49.18 41.70 49.18 41.70 49.18 41.70 49.18 41.70 49.29  41.85 49.29 41.85 49.29	age of absolute absolute alcohol by weight.  39.85 39.95 47.18 39.95 47.29 40.00 47.35 40.05 47.40 40.15 47.51 40.20 47.56 40.25 47.62 40.30 47.67  40.85 47.62 40.40 47.78 40.45 47.83 40.55 47.83 40.55 47.94 40.65 47.99 40.65 40.70 48.10 40.75 48.16 40.80 48.21  40.85 40.70 48.10 40.75 48.16 40.80 48.21  40.85 40.90 48.32 40.96 40.90 48.32 40.96 40.90 48.32 40.96 40.90 48.32 41.00 48.64 41.15 48.59 41.20 41.35 48.80 41.40 48.86 41.45 49.97 41.55 49.02 41.60 49.07 41.60 49.07 41.60 49.07 41.60 49.18 41.90 49.40 41.96	age of absolute alcohol by weight.         age of absolute alcohol by volume.         Specific absolute alcohol by weight.         age of absolute alcohol by weight.         age of absolute alcohol by weight.           39.85         47.18         0.9849         42.33           39.90         47.24         42.48         42.38           40.05         47.40         5         42.48           40.05         47.40         5         42.57           40.15         47.51         4         42.57           40.20         47.56         2         42.67           40.30         47.67         0         42.76           40.35         47.67         0         42.76           40.40         47.83         42.81         42.81           40.45         47.83         6         42.95           40.65         47.83         6         42.95           40.65         47.89         4         48.05           40.65         48.05         48.10         42.95           40.70         48.16         1         43.19           40.95         48.82         40.94         48.32           40.95         48.87         41.05         48.48           41.10	age of absolute alcohol by weight.    39.85	age of absolute alcohol by weight. below by it with the below by weight. below by it with the below by weigh	age of absolute alcohol by alcohol by weight.         age of absolute alcohol by weight.         age of absolute alcohol by weight.         Specific alcohol by weight.         age of also lute alcohol by weight.         Specific alcohol by weight.         age of alcohol by weight.         alcohol by alcohol by weight.         alcohol by weight.         alcohol by weight.         alcohol by weight.         alcohol by alcohol by weight.         alcohol by alcohol by weight.         alcohol by alcohol by

Percentage of Alcohol by Weight and by Volume from the Specific Gravity (at 15.5° C.), by Otto Hehner.—Continued.

	Percent-	Percent-		Percent-	Percent-		Percent-	Percent
Specific	age of	age of absolute	Specific	age of absolute	age of absolute	Specific	age of absolute	age of
gravity at 15.5° C.	absolute	absolute	gravity at	absolute	absolute	grāvity at	absolute	absolute
15.5° C.		alcohol by	15.5° C.		alcohol by	15.5° C.	alcohol by	
	weight.	volume.		weight.	volume.		weight.	volume
		\\	<u> </u>	ļ				
0.8890	62.82	70.35	40	77.71	83.60	0.8190	91.86	94.26
80	63.26	70.77	30	78.12	83.94	80	91.71	94.51
70		71.17	20	78.52	84.27	70	92.07	94.76
	63.70							
60	64.13	71.58	10	78.92	84.60	60	92.44	95.03
50	64.57	71.98	00	79.32	84.93	50	92.81	95.29
40	65.00	72.38				40	93.18	95.55
30	65.42	72.77	0.8490	79.72	85.26	30	93.55	95.82
20	65.83	73.15	80	80.18	85.59	20	93.92	96.08
10	66.26	78.54	70	80.54	85.94	10	94.28	96.32
00	66.70	73.93	60	80.96	86.28	00	94.62	96.55
1	1	10100	50	81.36	86.61		1 02:02	00.00
0.8790	67.13	74.88	40	81.76	86.93	0.8090	94.97	96.78
80	67.54	74.70	30	82.15	87.24	80	95.32	97.02
70		75.08	20	82.54				97.02
	67.96				87.55	70	95.68	
60	68.88	75.45	10	82.92	87.85	60	96.03	97.51
50	68.79	75.83	00	83.31	88.16	50	96.87	97.73
40	69.21	76.20	i	ł		40	96.70	97.94
80	69.63	76.57	0.8390	83.69	88.46	80	97.03	98.16
20	70.04	76.94	80	84.08	88.76	20	97.87	98.37
10	70-44	77.29	l) 70	84.48	89.08	10	97.70	98.59
00	70.84	77.64	60	84.88	89.89	l õõ	98.08	98.80
1	10.01		50	85.27	89.70		00.00	00.00
0.8690	71.25	78.00	40	85.65	89.99	0.7990	98.34	98.98
80	71.67	78.86	1 30	86.04	90.29	80	98.66	99.16
70		78.78	20	86.42				
	72.09				90.58	70	98.97	99.35
60	72.52	79.12	10	86.81	90.88	60	99.29	99.55
50	72.96	79.50	00	87.19	91.17	50	99.61	99.75
40	73.38	79.86	H	1		40	99.94	99.96
80	73.79	80.22	0.8290	87.58	91.46	11		
20	74.23	80.60	80	87.96	91.75	0.7939	99.97	99.98
10	74.68	81.00	70	88.36	92.05		Absolute	Alcoho
00	75.14	81.40	60	88.76	92.36	0.7938	100.00	100.00
]	1		50	89.16	92.66	31.030	-0000	-00.00
0 0000	MP PA	01 00				<b>11</b>	1	1
0.8590	75.59	81.80	40	89.54	92.94	Ħ	i	1
80		82.19	80	89.92	98.28	[]	1	1
70		82.54	20	90.29	93.49	ll	t	l
60		82.90	10	90.64	93.75	[]	1	]
50	77.29	83.25	<b>0</b> 0	91.00	94.00	ll	1	
1	1		H	1	I	11	1	1
				<del></del> -	• — —	· <u> </u>		

## V. Physical and Chemical Constants of Fixed Oils and Fats.

(From Lewkowitsch and other authorities.)

		r		
	Specific gravity at 15°C.	Specific gravity at 100°C.	Melting-point. C.	Solidifying-point. C.
Linseed oil	0.931-0.938 0.925-0.931	0.880	—16° to —26°	—16° —27° —27°
Walnut oil Poppy-seed oil	0.925-0.926 0.924-0.927	0.871 0.873		—27° —18°
Sunflower oil	0.924-0.926	0.919		17°
Fir-seed oil	0.925-0.928 0.921-0.926			—27° to —30° —10° to —15°
Cotton-seed oil	0.922-0.930	0.867		12°
Sesame oil	0.923-0.924 0.914-0.917	0.871 0.863		— 5° —2° to —10°
Black mustard oil	0.916-0.920	0.603		—17.5°
Croton oil	0.942-0.955			—16 ° —12° to —18°
Castor oil	0.960-0.966 0.915-0.919	0.910		—12°10 —18 —14°
Almond oil	0.915-0.920			10° to20°
Peanut (arachis) oil . Olive oil	0.916-0.920 0.914-0.917	0.867		-3° to -7°
Menhaden oil	0.927-0.933			-4°
Cod-liver oil	0.922-0.927 0.924-0.929	0.874 0.873		0° to10° 3°
Whale oil	0.920-0.930	0.872		2°
Dolphin oil	0.917-0.918 0.926	0.871		5° to —3° —16°
Porpoise oil	0.914-0.916	0.861		0° to 1.5°
Cotton-seed stearine .	0.919-0.923	0.867	40° 27° to 42°	31° to 32.5°
Palm oil	0.921-0.925 0.950-0.952	0.856 0.858	30° to 33°	25° to 26°
Cocoa-nutoil	0.925-0.926	0.873	20° to 26°	16° to 20°
Myrtle wax Japan wax	0.995 0.970-0.980	0.875 0.875	40° to 44° 51° to 54.5°	39° to 43° 46°
Lard	0.931-0.938	0.861	41° to 46°	29°
Bone fat	0.914-0.916 0.943-0.952	0.860	21° to 22° 42° to 46°	15° to 17° 35° to 37°
Butter fat	0.927-0.936	0.866	29.5° to 33°	19° to 20°
Oleomargarine	0.924-0.930 0.875-0.884	0.859		
Sperm oil	0.879-0.880	0.827		
Carnauba wax	0.990-0.999 0.973	0.842	84° to 85° 39° to 42°	80° to 81° 30° to 30.2°
Wool-fat	0.958-0.969	0.822	62° to 64°	60.5° to 62°
Spermaceti	0.960	0.812	43.5° to 49°	43.4° to 44.2° 80.5° to 81°
Chinese wax Tung (Chinese wood oil)	0.970 0.936-0.942	0.810	80.5° to 81°	below17°
Soya-bean oil	0.924-0.927			8° to 15°
	1	1	<u> </u>	1

# V. Physical and Chemical Constants of Fixed Oils and Fats.—Continued.

(From Lewkowitsch and other authorities.)

	Saponification value.	Maumené test.	Iodine value.	Hehner value.	Reicher value.
Linseed oil	190-195	104°-111°	175-190		
Hemp-seed oil	190-193	95°–96°	148		l
Walnut oil	195	96°-101°	144-147	l	
Poppy-seed oil	195	86°–88°	134141	95.38	l <b>.</b> .
Sunflower oil	193-194	72°–75°	120-129	95	١
Fir-seed oil	191.3	98°-99°	118.9-120		<i>.</i> .
Maize oil	188-193	56°-60.5°	117-125	89-95.7	2.5
Cotton-seed oil	191-195	68°-77°	104-110	96-17	
Sesame oil	189-193	64°-68°	105-109	95.8	0.35
Rape-seed oil	170-178	51°60°	95-105	95	
Black mustard oil	174-174.6	43°–44°	96°-110	95.05	
Croton oil	210.3-215		101.7-104	89	13.5
Castor oil	178-186	46°-47°	83.4-85.9		1.4
Apricot-kerneloil	192.2-193.1	42.5°-46°	100-107	• - : - •	
Almond oil	190.5-195.4	51°-54°	93-97	96.2	
Peanut (arachis) oil	190-197	45°-49°	85-98	95.86	
Olive oil	191-196	41.5°-45.5°	80.6-84.5	95.43	0.3
Menhaden oil	189.3-192	123°-128°	140–170	۰ ۔ ۔ .	1.2
Cod-liver oil	182–187	102°-103°	154–180	95.3	
Seal oil	190-196	92°	127-140	94.2	0.22
Whale oil.	188–193	91°–92°	110-136	93.5	2.04
Dolphin oil { Body oil .	197.3	• • • • •	99.5	93.07	5.6
(000), 000	200		32.8	66.28	65.92
Porpoise oil $\begin{cases} Bodyoil \\ Jaw oil \end{cases}$ .	216-218.8	50°	119.4	00.41	23.45
Jaw oil .	253.7	47°-48.5°	49.6	68.41	65.8
Neat's-foot oil	194.3 194.6–195.1	47°-48.5°	69.3–70.4 88.7–92.8	96.3	
Cotton-seed stearine .	194.6-195.1	48		1	0.5
Palm oil	190.5-202	• • • • •	53-57 32-41	95.6 94.59	1.6
Cocoa-nut oil	250-253	• • • • •	8.5-9.3	88.6	3.7
Myrtle wax	205.7-211.7		2.9	1	3.7
Japan wax	220-222.4		4.2-8.5	90.6	• •
Lard	195.3-196.6	27°-32°	57-70	96	
Bone fat	190.9	21 -02	46.3-49.6	00	
Tallow	195-198	1	36-47	95.6	0.25
Butter fat	221.5-227		26-35	87.5	28.78
Oleomargarine	194-203.7	1	55.3-60	95-96	2.6
Sperm oil	132.5-147	47°-51°	84	00-00	1.3
Bottle-nose oil	126-134	41°-47°	77.4-82	1	1.4
Carnauba wax	80-84	1	13.5	1: : :	1
Wool-fat	98.2-102.4	1	25-28	: : :	: :
Beeswax	91-96		8.3-11	11. 1. 1	
Spermaceti	128			I	
Chinese wax	63		1	1. : :	1 : :
Tung (Chinese wood oil)	1	1	150-165	1. : :	1::
Soya-bean oil	190.6-192.9	59°-61°	121.3-124	95.5	
	1			1	• •

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